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X-ray Structure Analysis of Cubic Tetracyanoethylene and the Length of the C≡N Bond. Application of a Double-Atom Refinement Method

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The crystal structure of a cubic modification of tetracyanoethylene has been studied. The space group is *Im*3 and the cell edge is 9·736 (5) Å. The bond lengths agree well with those in the monoclinic modification, but there are significant differences between the bond angles in the two forms. The central C=C bond is 1·344 (2) Å which is not significantly different from the corresponding bond length in ethylene and considerably shorter than predicted from INDO calculations. A new double-atom refinement method has been applied which, from the X-ray data alone, corrects for the apparent shortening of the C≡N bond length, as previously found by comparison of X-ray and neutron diffraction data. The corrected value for C≡N (1·166 (2) Å) is close to the electron diffraction result on tetracyanoethylene. The molecular packing in the crystal is such that large cavities surround the positions (0,0,0) and ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$).

Introduction

Tetracyanoethylene (TCNE) is a compound of considerable interest, as it forms charge-transfer complexes with a large number of organic molecules.

As part of a research program on the charge distribution in aromatic hydrocarbon molecules and their charge-transfer complexes with TCNE, we have made a study of a cubic modification of tetracyanoethylene, crystals of which were obtained accidentally during an attempt to prepare some charge-transfer complexes. The cubic form of TCNE has not been described in the scientific literature, but we discovered after a substantial part of this work had been completed that it had been studied several years ago by Coulter & Trueblood (1963). The present results are fully compatible with those obtained earlier, but no detailed comparison between the two data sets has been attempted.

A monoclinic modification of TCNE has been described by Bekoe & Trueblood (1960, 1964), while Hope (1968) performed an electron diffraction analysis of the molecule in the gas phase. The thermodynamic relationship between the two solid modifications is not known.

Experimental

A large mass of the cubic form of TCNE was obtained from ethyl acetate solutions. When a saturated solution in the same solvent was seeded with this material, nicely formed cubic crystals of TCNE showing the form {100} were obtained. The density was determined as 1·375 g.cm^{-3} by flotation in hexane–carbon tetrachloride mixtures. This compares with a measured density of 1·318 g.cm^{-3} for the monoclinic modification, indicating that the molecules are more closely packed in the cubic form.

There are six molecules in the body-centered unit cell, while the Laue symmetry of the X-ray photographs is *m*3. The only cubic space groups compatible with the body-centering and the Laue symmetry, which will accommodate six molecules of TCNE in the unit cell are *I*23 (no. 197) and *Im*3 (no. 204). The latter centric space group was selected on the basis of the structure analysis. Crystallographic data are summarized in Table 1.

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Table 1. *Crystallographic data on the cubic form of TCNE*

Space group	$Im3$
a	$9{\cdot}736 \pm 0{\cdot}006$ Å
Z	6
D_x	$1{\cdot}383$ g.cm^{-3}
D_m	$1{\cdot}375$

Intensity data were collected on a Picker automatic diffractometer with a capillary-sealed crystal of dimensions $0{\cdot}35 \times 0{\cdot}35 \times 0{\cdot}41$ mm, mounted in an arbitrary orientation to avoid systematic multiple reflection. A total of 3119 reflections (including many symmetry-equivalent sets) were measured with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) at room temperature (25 °C). Reflections were observed up to $\sin\theta/\lambda = 0{\cdot}94$ Å^{-1}, indicating that thermal motion in the crystal is relatively small.

Data reduction

A trial calculation showed that absorption was constant within 0·5 %. Since the experimental errors in the intensity data are several times greater, no absorption corrections were applied.

Up to twelve symmetry-equivalent reflections were measured in the low-order region, while all but 161 high order intensities were measured more than once. To reduce the more than 3000 reflections to a unique set an average $\langle I\rangle$ was calculated from each form $\{hkl\}$ and its standard deviation $\sigma(\langle I\rangle)$ taken as $[\sum(I-\langle I\rangle)^2/(n-1)]^{1/2}$ in which n is the number of measurements included in the average.

Subsequently, those intensities which deviated by more than one standard deviation from the average $\langle I\rangle$ were eliminated and the average and its standard deviation recalculated. In this way, a number of obviously erroneous measurements were excluded. The agreement factor $\frac{\sum|F^2-\langle F^2\rangle|}{\sum F^2}$ over all included reflections was calculated as 1·8 %. The standard deviation of reflections observed only once was obtained from the expression

$$\sigma^2(I-B) = (0{\cdot}03)^2(I-B)^2 + (I+B)\,.$$

Since these reflections are all very weak, the statistical contribution (*i.e.* the last term) is dominant. 351 of the 706 unique reflections were smaller than four times the standard deviation. They were treated as unobserved reflections in the refinement of the structure.

Solution and refinement of the structure

In both space groups permitted by the absences the molecular center has to be in the sixfold position at the center of the faces of the cube. The symmetry of this site is 222 in $I23$ and mmm in $Im3$. Since the TCNE molecules are not likely to be twisted around the central bond the latter space group was preferred. Within the restrictions imposed by the mmm site symmetry the double bond can be parallel to either of the three cubic axis. The two orientations of the molecular plane for each of the double bond directions can be shown to correspond merely to an interchange of crystallographic axes. Accordingly, there are three different symmetry-permitted models. Atomic coordinates for each of these were derived with the molecular dimensions of the monoclinic form (Bekoe & Trueblood, 1960). One model (Fig. 2) converged rapidly.

In the least-squares refinement reflections were considered unobserved whenever $F_{\rm obs} < F_t$, where F_t is the threshold value. F_t was taken as $4\sigma(F_{\rm obs})$ and such unobserved reflections were included with $F_{\rm obs} = F_t$ only if $F_{\rm calc} > F_t$. In the final cycles all unobserved reflections were calculated below the threshold and therefore excluded from the refinement. 355 reflections were observed and used to refine 18 parameters, including the scale factor, 5 positional, 11 temperature parameters, and an isotropic extinction parameter. Scattering factors were used as listed in *International Tables for X-ray Crystallography* (1962) for C (ground state) and N. Final agreement factors, parameters and a list of observed and calculated structure factors and extinction corrections are given in Tables 2, 3 and 4 respectively.

Molecular dimensions and packing

Intramolecular bond lengths and angles in the two TCNE modifications and the results of the gas-phase electron diffraction study are listed in Table 5. The bond distances and angles in cubic TCNE are shown in Fig. 1.

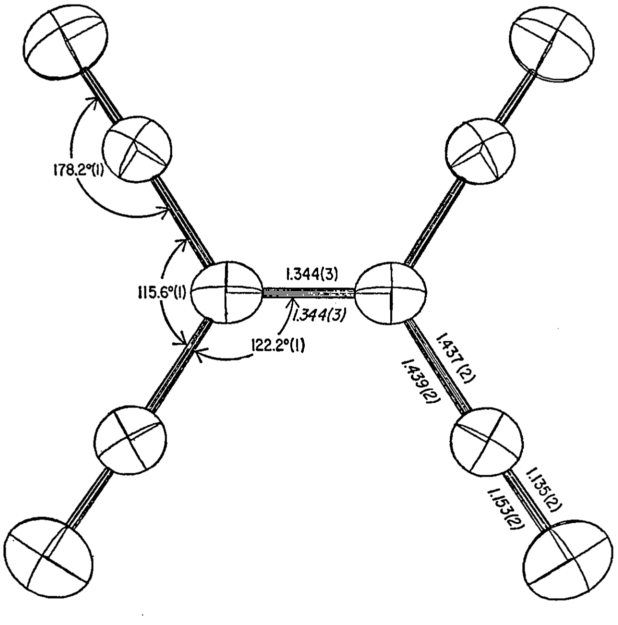

Fig. 1. Bond distances and angles in the cubic form of tetracyanoethylene. Values in italics are corrected for thermal motion. See Table 5 for values corrected for bonding effects.

Table 2. *Agreement factors* (%)

	Conventional least-squares		Double-atom refinement	
	All data	$\sin\theta/\lambda > 0{\cdot}6$	STO	HF
R	5·9	6·5	4·8	5·5
Rw	4·8	3·5	3·5	4·0
Number of observations	355	203	356	356
Number of variables	18	18	26	26

The similarity between the bond lengths in the two solid polymorphs is striking, the only significant difference being in the angles, in particular the C–C–C angle, which is closer to 120° in the monoclininc form. Thus, the value for the central C–C double bond length confirms the results of the more recent diffractometer study on monoclinic TCNE (Bekoe & Trueblood, 1964), in contrast to the earlier value of 1·317(9) Å obtained with visually estimated data (Bekoe & Trueblood, 1960). Both new values are within experimental errors of the C=C bond length in ethylene (1·333–1·337 Å) (Lide, 1962).

Coulter & Trueblood (1963) noted that the double bond is shorter than predicted by π-molecular orbital calculations. More recent all-valence electron calculations using the INDO approximation (Intermediate Neglect of Differential Overlap) (McIver, unpublished), do not remove the discrepancy. Use of an empirical bond order–bond length curve for the INDO results leads to a calculated C=C bond length of 1·375 Å, about 0·03 Å longer than actually observed.

Agreement with the electron diffraction results is

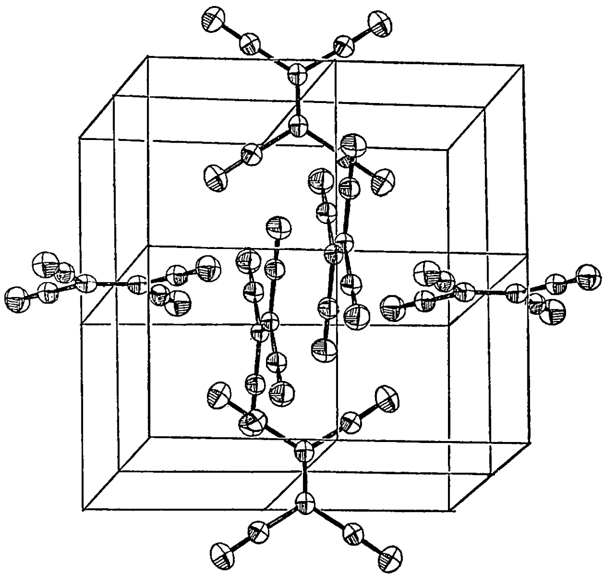

Fig. 2. Molecular packing. Only the molecules at the center of the cube faces are shown. Other symmetry-related molecules are centered at the mid points of the edges. The six molecules shown line a cavity at the middle of the unit cell·

Table 3. *Positional and thermal parameters*

Positional parameters are in fractions of the unit cell edge. Thermal parameters are the β_{ij} in the following expression for the temperature factor: $\exp\,[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+2hk\beta_{12}+2hl\beta_{13}+2hk\beta_{23})]$

				Double atom, HF valence shell		Double atom, STO valence shell	
		All data	$\sin\theta/\lambda > 0{\cdot}6$	Core	Valence shell	Core	Valence shell
N	*x*	0·21287 (14)	0·21273 (21)	0·21361 (17)	0·20910 (66)	0·21334 (15)	0·20992 (52)
	y	0·5	0·5	0·5	0·5	0·5	0·5
	z	0·72160 (12)	0·72262 (17)	0·72254 (16)	0·71756 (70)	0·72246 (14)	0·71787 (54)
C(2)	*x*	0·14768 (12)	0·14698 (14)	0·14733 (11)	0·14821 (74)	0·14737 (10)	0·14766 (58)
	y	0·5	0·5	0·5	0·5	0·5	0·5
	z	0·62490 (12)	0·62450 (15)	0·62458 (12)	0·62429 (95)	0·62460 (11)	0·62386 (72)
C(1)	*x*	0·06901 (16)	0·06949 (18)	0·06968 (16)	0·06976 (97)	0·06970 (16)	0·06976 (73)
	y	0·5	0·5	0·5	0·5	0·5	0·5
	z	0·5	0·5	0·5	0·5	0·5	0·5
N	β11	0·01042 (15)	0·00964 (18)	0·01006 (13)		0·00944 (12)	
	22	0·00987 (14)	0·00954 (20)	0·00967 (11)		0·00902 (10)	
	33	0·00822 (14)	0·00666 (16)	0·00788 (13)		0·00726 (12)	
	12	0·0	0·0	0·0		0·0	
	13	−0·00196 (9)	−0·00278 (11)	−0·00210 (8)		−0·00210 (7)	
	23	0·0	0·0	0·0		0·0	
C(2)	β11	0·00708 (13)	0·00679 (17)	0·00703 (11)		0·00654 (11)	
	22	0·00652 (12)	0·00629 (17)	0·00648 (12)		0·00601 (11)	
	33	0·00609 (12)	0·00507 (15)	0·00605 (11)		0·00557 (10)	
	12	0·0	0·0	0·0		0·0	
	13	0·00016 (10)	−0·00066 (9)	0·00010 (8)		0·00004 (7)	
	23	0·0	0·0	0·0		0·0	
C(1)	β11	0·00726 (17)	0·00557 (18)	0·00691 (14)		0·00640 (13)	
	22	0·00518 (14)	0·00547 (17)	0·00510 (12)		0·00472 (11)	
	33	0·00524 (15)	0·00462 (15)	0·00524 (13)		0·00482 (12)	
	12	0·0	0·0	0·0		0·0	
	13	0·0	0·0	0·0		0·0	
	23	0·0	0·0	0·0		0·0	

good, except for the $C\equiv N$ bond which even after correction for apparent shortening due to thermal motion, remains 0·009 (3) Å shorter than the electron diffraction value. The difference is small, but it should be pointed out that better agreement is obtained when the high order data only are used in the refinement or when the core and valence shell centers are refined separately (Coppens, 1970), as discussed below.

The molecular packing in the structure is of interest. As shown in Fig. 2 the double bonds of all six molecules at the midpoints of the cube face point toward the center of the unit cell. As a result, a large hole exists centered at $\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$ (and at the symmetry related 0,0,0 position) and surrounded by a cage of 6 $N\equiv C–C–C\equiv N$ groupings. The distance between two diametrically opposed nitrogen atoms of the cage is 7·4 Å, more than four times the nitrogen van der Waals radius, thus leading to the speculation that a noble gas atom or small ion might be occluded without disturbing the crystal structure.

Nevertheless, the cubic form has the higher density of the two forms; therefore, the packing must be reasonably efficient. No abnormally short intermolecular distances exist, the shortest being 3·185 (2) Å between a nitrogen atom and a C(2) atom of adjacent molecules, while all other intermolecular distances are larger than 3·4 Å. It seems that the efficiency of the packing in the cube faces is made possible by the perpendicular arrangement of the double bonds and the peculiar shape of the molecules, the 'arms' of one molecule embracing the double bond of its neighbors, as illustrated in Fig. 3.

The difference between the C–C–C angles in the cubic and the monoclinic forms can be traced to the lack of contact distances on the 'open' side of the nitrogen in the cubic form which leads to a deformation of the C–C–C angle.

The decrease in C–C–C angle is accompanied by a bending of the $C–C\equiv N$ angle. Both deformations are such as to decrease the $N\cdots N$ non-bonded intramolecular distance within the $N\equiv C–C–C\equiv N$ group. It is 4·31 Å; or about 0·11 Å less than in the monoclinic form.

It is worth while to note that the molecule is almost a square as the intramolecular $N\cdots N$ vectors parallel to the double bonds have a length of 4·14 Å.

The effect of bonding on the $C\equiv N$ distance

X-ray positions for terminal atoms may deviate significantly from the nuclear position. Thus, approximate

Table 4. *Observed and calculated structure factors* (×10)

The column headed EXT lists the reduction in intensity due to extinction. The values of F_{obs} have been corrected for this effect. A negative value of F_{obs} indicates the threshold value for an unobserved reflection.

L= 0

K	H	FOBS	FCALC	EXT
0	2	4084	4174	61
0	4	7430	7540	52
0	6	4346	4216	81
0	8	3953	3938	86
0	10	1728	1789	97
0	12	498	510	
0	14	1586	1600	98
0	16	483	513	
0	18	436	364	
1	1	3663	3600	60
1	3	9810	9680	39
1	5	995	890	99
1	7	1657	1632	97
1	9	-248	245	
1	11	1378	1450	98
1	13	-169	9	
1	15	-202	55	
1	17	260	185	
1	19	-203	80	
2	2	1147	1100	96
2	4	2374	2346	90
2	6	616	598	99
2	8	653	701	99
2	10	378	402	
2	12	439	380	
2	14	526	509	
2	16	-212	83	
2	18	-192	5	
3	3	1042	997	98
3	5	2767	2762	90
3	7	369	316	
3	9	470	503	
3	11	514	460	
3	13	737	722	
3	15	281	189	
3	17	-349	196	
3	19	-287	110	
4	4	2359	2422	92
4	6	205	189	
4	8	752	859	99
4	10	-183	187	
4	12	-213	121	
4	14	664	584	
4	16	346	329	
4	18	-232	2	
5	5	579	571	
5	7	1929	2013	96
5	9	-97	105	
5	11	1129	1117	99
5	13	439	356	
5	15	-191	67	
5	17	-204	188	
6	6	265	249	
6	8	246	197	
6	10	567	553	
6	12	387	309	
6	14	-266	319	
6	16	-139	60	
6	18	-246	31	
7	7	200	155	
7	9	743	756	
7	11	773	831	
7	13	416	372	
7	15	-164	31	
7	17	-164	195	
8	8	575	606	
8	10	271	284	
8	12	-205	163	
8	14	587	536	
8	16	-222	150	
9	9	946	987	94
9	11	1071	1022	99
9	13	-157	98	
9	15	-306	264	
9	17	-327	286	
10	10	-125	75	
10	12	345	306	
10	14	-367	351	
10	16	-283	99	
11	11	-197	96	
11	13	402	326	
11	15	-161	57	
12	12	-208	43	
12	14	-199	104	
13	13	-177	41	

L= 1

K	H	FOBS	FCALC	EXT
0	3	4724	4720	65
0	5	858	838	94
0	7	1446	1442	97
0	9	1196	1240	99
0	11	993	991	99
0	13	653	691	
0	15	296	198	
0	17	-263	96	
0	19	-185	116	
1	2	4430	4328	66
1	4	3863	3707	79
1	6	1870	1798	96
1	8	2202	2271	95
1	10	1450	1522	98
1	12	274	287	
1	14	232	183	
1	16	398	638	
1	18	-278	263	
2	3	4412	4218	73
2	5	651	683	94
2	7	903	968	99
2	9	462	423	
2	11	812	799	
2	13	526	474	
2	15	-171	163	
2	17	-101	10	
2	19	-267	16	
3	4	1863	1732	95
3	6	580	581	
3	8	725	729	99
3	10	544	544	
3	12	508	519	
3	14	365	328	
3	16	-174	27	
3	18	-154	26	
4	5	1660	1624	97
4	7	1289	1363	98
4	9	274	226	
4	11	262	271	
4	13	-147	82	
4	15	364	314	
4	17	-195	76	
5	6	548	609	
5	8	-231	180	
5	10	410	427	
5	12	269	213	
5	14	257	171	
5	16	247	94	
5	18	-207	48	
6	7	-138	80	
6	9	-120	43	
6	11	389	341	
6	13	728	705	
6	15	368	233	
6	17	-158	1	
7	8	727	803	99
7	10	386	400	
7	12	264	160	
7	14	384	283	
7	16	-347	275	
7	18	-117	4	
8	9	549	482	
8	11	458	409	
8	13	837	781	
8	15	-247	273	
8	17	-268	135	
9	10	584	635	
9	12	-107	137	
9	14	-217	24	
9	16	-147	20	
10	11	-204	28	
10	13	-147	116	
10	15	359	291	
11	12	283	161	
11	14	325	141	
12	13	295	155	
12	15	-149	3	
13	14	-172	11	

L= 2

K	H	FOBS	FCALC	EXT
0	4	3035	3002	85
0	6	1818	1805	96
0	8	700	723	99
0	10	334	363	
0	12	281	286	
0	14	-305	246	
0	16	355	281	
0	18	-254	123	
1	3	2406	2297	89
1	5	1754	1747	95
1	7	1309	1345	98
1	9	-143	104	
1	11	-185	99	
1	13	-255	173	
1	15	321	243	
1	17	-249	202	
1	19	-267	38	
2	2	11331	11498	34
2	4	880	790	99
2	6	2402	2421	93
2	8	827	842	99
2	10	337	320	
2	12	1263	1240	99
2	14	-164	196	
2	16	429	398	
2	18	-242	63	
3	3	2075	2007	93
3	5	3179	3108	88
3	7	470	485	
3	9	2200	2269	96
3	11	533	417	
3	13	-108	43	
3	15	-66	185	
3	17	-321	147	
3	19	-159	26	
4	4	497	545	
4	6	740	753	99
4	8	858	906	99
4	10	230	230	
4	12	592	565	
4	14	-223	180	
4	16	227	59	
4	18	-155	41	
5	5	528	510	
5	7	579	619	
5	9	289	306	
5	11	343	342	
5	13	268	127	
5	15	-250	150	
5	17	-74	32	
6	6	-56	30	
6	8	603	406	
6	10	313	307	
6	12	-199	118	
6	14	-38	17	
6	16	288	237	
6	18	-183	12	
7	7	230	219	
7	9	1254	1216	99
7	11	359	369	
7	13	629	544	
7	15	-182	4	
7	17	-276	14	
8	8	357	294	
8	10	366	337	
8	12	-234	82	
8	14	-138	73	
8	16	-89	80	
9	9	-217	194	
9	11	-174	19	
9	13	254	142	
9	15	-214	55	
9	17	-215	37	
10	10	304	142	
10	12	368	339	
10	14	-249	49	
10	16	-228	46	
11	11	-147	30	
11	13	-124	28	
11	15	-161	111	
12	12	317	283	
12	14	-208	113	
13	13	-240	30	

L= 3

K	H	FOBS	FCALC	EXT
0	5	4926	4874	76
0	7	2474	2473	94
0	9	3014	3059	92
0	11	348	248	
0	13	661	672	
0	15	364	429	
0	17	304	232	
0	19	-219	119	
1	4	1356	1281	97
1	6	417	408	
1	8	1060	1105	99
1	10	244	205	
1	12	534	489	
1	14	-231	153	
1	16	-51	61	
1	18	-134	13	
2	5	517	574	
2	7	1001	995	99
2	9	673	682	
2	11	-157	25	
2	13	-97	36	
2	15	-142	66	
2	17	-194	148	
2	19	-280	47	
3	4	2518	2426	92
3	6	2855	2814	92
3	8	651	653	
3	10	665	507	
3	12	736	798	
3	14	318	333	
3	16	-179	89	
3	18	-158	53	
4	5	1532	1547	97
4	7	988	1059	99
4	9	224	274	
4	11	630	635	
4	13	-209	85	
4	15	467	393	
4	17	394	327	
5	6	415	370	
5	8	691	633	
5	10	-114	18	
5	12	206	151	
5	14	285	264	
5	16	300	191	
5	18	-67	54	
6	7	403	405	
6	9	-130	59	
6	11	883	824	
6	13	361	296	
6	15	-213	134	
7	8	573	576	
7	10	475	460	
7	12	549	496	
7	14	-296	199	
7	16	-165	20	
8	9	388	370	
8	11	-14	106	
8	13	-172	16	
8	15	-180	74	
8	17	-251	55	
9	10	533	447	
9	12	659	342	
9	14	-126	68	
9	16	402	300	
10	11	-259	191	
10	13	283	168	
10	15	-163	199	
11	12	361	327	
11	14	-158	119	
12	13	329	158	
13	14	-243	119	

L= 4

K	H	FOBS	FCALC	EXT
0	6	1873	1822	98
0	8	-193	158	
0	10	904	898	99
0	12	744	751	
0	14	-206	158	
0	16	289	189	
0	18	-166	115	
1	5	1959	1917	95
1	7	887	911	99
1	9	1640	1651	98
1	11	487	482	
1	13	223	141	
1	15	449	429	
1	17	418	340	
2	6	1257	1231	98
2	8	1409	1402	98
2	10	528	499	
2	12	-144	112	
2	14	-142	141	
2	16	-238	170	
2	18	-78	16	
3	5	850	855	99
3	7	1943	2035	96
3	9	491	499	
3	11	809	727	
3	13	-128	93	
3	15	-169	30	
3	17	-153	28	
4	4	4597	4558	81
4	6	360	364	
4	8	682	698	
4	10	1214	1210	99
4	12	445	392	
4	14	354	303	
4	16	-207	25	
4	18	-174	140	
5	5	-118	65	
5	7	3170	3191	92
5	9	-128	38	
5	11	531	531	
5	13	-240	266	
5	15	-347	186	
5	17	-24	20	
6	6	1530	1552	98
6	8	573	564	
6	10	-137	97	
6	12	472	487	
6	14	-213	201	
6	16	-202	117	
7	7	-116	41	
7	9	426	461	
7	11	388	330	
7	13	-392	279	
7	15	342	256	
7	17	-145	160	
8	8	1132	1108	99
8	10	-182	71	
8	12	460	566	
8	14	-287	265	
8	16	-200	32	
9	9	228	224	
9	11	-123	93	
9	13	-191	38	
9	15	-201	1	
10	10	215	213	
10	12	-196	94	
10	14	-152	9	
10	16	-176	64	
11	11	-301	198	
11	13	-177	19	
11	15	-184	33	
12	12	-196	93	
12	14	-142	41	
13	13	-254	119	

L= 5

K	H	FOBS	FCALC	EXT
0	7	1528	1569	98
0	9	885	849	99
0	11	413	579	
0	13	-193	117	
0	15	-223	160	
0	17	-187	129	
1	6	1274	1364	98
1	8	1342	1391	98
1	10	336	292	
1	12	-153	58	
1	14	-176	23	
1	16	-149	56	
1	18	-156	12	
2	7	3384	3428	90
2	9	179	122	
2	11	906	893	99
2	13	277	316	
2	15	-200	174	
2	17	-261	37	
3	6	915	933	99
3	8	507	490	
3	10	631	660	
3	12	413	375	
3	14	-238	217	
3	16	-226	209	
3	18	-205	109	
4	7	228	188	
4	9	570	573	
4	11	-134	101	
4	13	-182	198	
4	15	328	205	
4	17	-151	156	
5	6	614	637	
5	8	576	586	
5	10	377	364	
5	12	-133	63	
5	14	-181	19	
5	16	344	196	
5	18	-163	44	
6	7	1743	1744	98
6	9	-168	65	
6	11	-184	192	
6	13	-201	85	
6	15	-145	17	
6	17	-180	10	
7	8	-165	108	
7	10	879	885	99
7	12	563	486	
7	14	477	382	
7	16	-153	36	
8	9	291	205	
8	11	-204	129	
8	13	-219	149	
8	15	-141	2	
9	10	-216	200	
9	12	-161	22	
9	14	-91	28	
9	16	-287	178	
10	11	-164	15	
10	13	-269	186	
10	15	-231	119	
11	12	-183	60	
11	14	330	125	
12	13	-154	32	

L= 6

K	H	FOBS	FCALC	EXT
0	8	1118	1120	99
0	10	-226	197	
0	12	-118	50	
0	14	399	351	
0	16	301	248	
0	18	-287	123	
1	7	507	491	
1	9	337	306	
1	11	-145	9	
1	13	-312	222	
1	15	-267	225	
1	17	-290	190	
2	8	340	391	
2	10	342	341	
2	12	472	413	
2	14	-92	78	
2	16	-169	83	
2	18	-122	66	
3	7	587	562	
3	9	479	436	
3	11	906	918	99
3	13	490	521	
3	15	-268	169	
3	17	-61	86	
4	8	1409	1447	98
4	10	754	744	
4	12	-134	88	
4	14	-203	142	
4	16	323	298	
5	7	-62	42	
5	9	477	422	
5	11	-148	107	
5	13	512	442	
5	15	-142	105	
5	17	-269	118	
6	6	1011	935	99
6	8	212	193	
6	10	688	692	
6	12	327	285	
6	14	286	188	
6	16	-66	21	
7	7	270	232	
7	9	531	531	
7	11	-223	200	
7	13	333	270	
7	15	-125	69	
7	17	-40	35	
8	8	-138	97	
8	10	-221	147	
8	12	-182	52	
8	14	-279	12	
8	16	-195	66	
9	9	232	205	
9	11	-266	78	
9	13	-214	121	
9	15	-141	66	
10	10	355	317	
10	12	-217	81	
10	14	-159	44	
11	11	342	299	
11	13	-251	235	
13	13	-185	104	

L= 7

K	H	FOBS	FCALC	EXT
0	9	1991	1994	97
0	11	263	211	
0	13	-179	74	
0	15	-217	135	
0	17	-89	187	
1	8	740	740	
1	10	813	823	
1	12	327	307	
1	14	-181	26	
1	16	-210	104	
1	18	-200	92	
2	9	341	350	
2	11	487	441	
2	13	-151	128	
2	15	-264	38	
2	17	-131	78	
3	8	975	969	99
3	10	237	202	
3	12	-148	143	
3	14	329	334	
3	16	324	235	
4	9	1415	1422	99
4	11	719	730	
4	13	425	422	
4	15	-206	96	
4	17	-162	109	
5	8	944	970	99
5	10	302	276	
5	12	792	794	
5	14	401	374	
5	16	359	313	
6	9	580	579	
6	11	-220	171	
6	13	308	293	
6	15	-282	19	
6	17	-226	89	
7	8	482	483	
7	10	375	357	
7	12	354	316	
7	14	258	190	
7	16	-198	83	
8	9	-141	141	
8	11	-235	176	
8	13	409	345	
8	15	-261	81	
9	10	-228	125	
9	12	295	253	
9	14	294	123	
10	11	-277	141	
10	13	-126	86	
10	15	-258	79	
11	14	-134	148	
12	13	-105	24	

L= 8

K	H	FOBS	FCALC	EXT
0	10	-179	171	
0	12	275	245	
0	14	492	408	
0	16	-125	90	
1	9	245	253	
1	11	-188	100	
1	13	394	353	
1	15	411	320	
1	17	-96	68	
2	10	416	396	
2	12	-188	237	
2	14	-278	154	
2	16	-268	1	
3	9	514	480	
3	11	544	482	
3	13	510	501	
3	15	338	200	
3	17	-140	45	
4	10	657	494	
4	12	-213	103	
4	14	-102	78	
4	16	-210	274	
5	9	-196	114	
5	11	-249	137	
5	13	440	399	
5	15	-270	135	
6	10	573	401	
6	12	315	277	
6	14	-104	19	
6	16	-65	31	
7	9	419	396	
7	11	-252	249	
7	13	-166	81	
7	15	307	142	
8	8	342	277	
8	10	437	349	
8	12	317	192	
8	14	-209	44	
9	9	265	166	
9	11	-209	109	
9	13	-272	201	
9	15	-143	32	
10	10	310	310	
10	12	-157	63	
10	14	-214	67	
11	11	-228	106	
11	13	-268	211	

L= 9

K	H	FOBS	FCALC	EXT
0	11	-218	145	
0	13	-142	32	
0	15	-160	129	
0	17	367	235	
1	10	-129	124	
1	12	-157	118	
1	14	365	252	
1	16	-117	88	
2	11	804	793	
2	13	-211	6	
2	15	-294	52	
2	17	-163	129	
3	10	-158	60	
3	12	343	279	
3	14	368	297	
3	16	-262	45	
4	11	-204	159	
4	13	-151	103	
4	15	357	206	
5	10	-171	136	
5	12	-34	18	
5	14	305	186	
5	16	-281	66	
6	11	-16	71	
6	13	344	227	
6	15	-240	36	
7	10	321	343	
7	12	459	386	
7	14	413	421	
8	11	-258	179	
8	13	296	157	
8	15	-143	4	
9	10	-161	1	
9	12	-126	75	
9	14	-239	178	
10	11	-266	141	
10	13	-231	9	

L= 10

K	H	FOBS	FCALC	EXT
0	12	-267	286	
0	14	-188	126	
0	16	-152	52	
1	11	-237	137	
1	13	376	305	
1	15	-283	243	
2	12	261	144	
2	14	-178	26	
2	16	-137	31	
3	11	-216	156	
3	13	297	145	
3	15	-121	31	
4	12	418	314	
4	14	-145	223	
4	16	-258	20	
5	11	390	368	
5	13	-223	16	
5	15	-179	88	
6	12	233	221	
6	14	-225	55	
7	11	-197	20	
7	13	-138	2	
7	15	-235	129	
8	12	-207	246	
8	14	-125	92	
9	11	-197	14	
9	13	-224	125	
10	10	-162	115	

L= 11

K	H	FOBS	FCALC	EXT
0	13	268	196	
0	15	-268	187	
1	12	-262	218	
1	14	-112	93	
2	13	-223	33	
2	15	-188	12	
3	12	-238	215	
3	14	-250	126	
4	13	-136	32	
4	15	-260	127	
5	12	-309	130	
5	14	-132	75	
6	13	-221	118	
7	14	-168	71	
8	13	-205	46	

L= 12

K	H	FOBS	FCALC	EXT
0	14	-193	55	
1	13	-207	83	
1	15	-245	93	
2	14	-184	4	
3	13	-193	65	
4	14	-193	49	
5	13	-225	59	
7	13	-302	258	

L= 13

K	H	FOBS	FCALC	EXT
1	14	-245	127	
3	14	-168	28	

calculations with Slater orbitals have shown that the centroid of an oxygen atom of a nitro group is displaced outwards, away from the nitrogen atom (Coppens & Coulson, 1967). Similar calculations for C≡N indicate a much smaller displacement of the nitrogen charge center (Coppens, unpublished), because the C≡N is a stronger and shorter bond than N–O.

A more conclusive answer on the direction of the shift and its size in the case of –C≡N is provided by the combined X-ray and neutron analyses on tetracyanoethylene oxide (TCNO) by Matthews, Swanson & Stucky (1970).

The average over the four C≡N bond lengths in this structure is 0·009 Å shorter when measured with X-rays than when measured with neutrons (X-ray average 1·129 Å, neutron average 1·138 Å). Further analysis of the positional parameters shows that the average positions of the carbon and the nitrogen atoms are slightly displaced towards the center of the triple bond. Thus, the results on TCNO support evidence on discrepancies between X-ray and neutron parameters summarized earlier (Coppens, Sabine, Delaplane & Ibers, 1969).

In the absence of neutron data, we have used two alternative methods to study this effect in cubic TCNE. First, in a high-order refinement all reflections with $\sin\theta/\lambda$ smaller than 0·6 Å^{-1} were excluded from the least-squares refinement.

The second method is a double-atom refinement technique in which the occupancy of the *K*-shell and the positions of the *K*- and the *L*-shells are refined separately, while the two shells retain a common temperature parameter (Coppens, 1970). Though this method does not account for deviations from spherical symmetry of the valence shell, it allows the centroids of the two parts of the atom to have different positions. Thus, the *K*-shell centroid should correspond closely with the nuclear position as determined by neutrons, while the *L*-shell would be displaced considerably in the direction

Table 5. *Intramolecular distances and angles in tetracyanoethylene*

	Cubic TCNE all data		Monoclinic TCNE (Bekoe & Trueblood, 1963)	Gas phase (Hope, 1968)	Cubic TCNE			
					$\sin\theta/\lambda > 0{\cdot}6$ Å^{-1}		Double atom refinement (average over STO and HF)	
	Uncorrected	Corrected (riding model)	Uncorrected		Uncorrected	Corrected (riding model)	Uncorrected	Corrected (riding model)
C≡N	1·135 (2) Å	1·153 (2) Å	1·135 Å 1·133	1·162 (2) Å	1·150 (2) Å	1·166 (2) Å	1·150 (2) Å	1·166 (2) Å
C–C	1·437 (2)	1·439 (2)	1·442	1·435 (10)	1·428 (2)	1·432 (2)	1·429 (2)	1·433 (2)
C=C	1·344 (3)	1·344 (3)	1·339	1·357 (10)	1·353 (3)	1·353 (3)	1·357 (3)	1·357 (3)
C–C≡N	178·2 (1)°		179·1° 179·4		178·1 (2)°			
C=C–C	122·2 (1)		121·0 120·9	121·1°	121·9 (1)			
C–C–C	115·6 (1)		118·1		116·2 (2)			

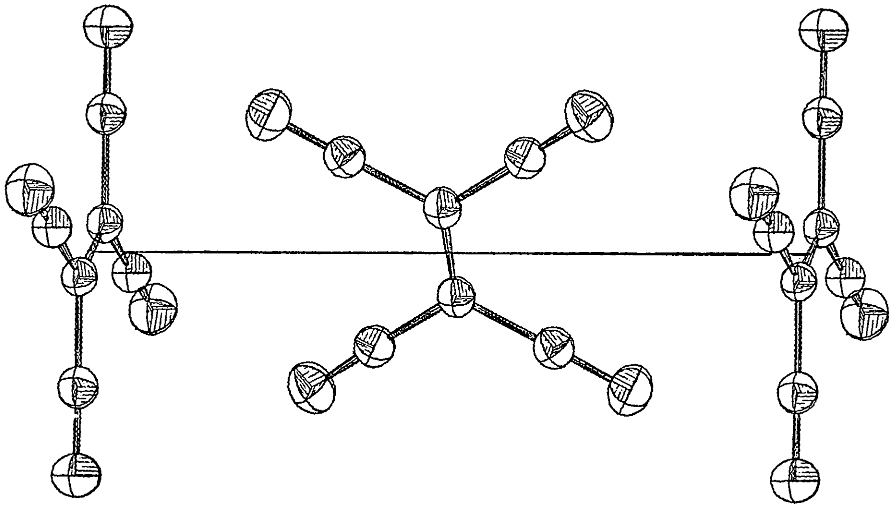

Fig. 3. The close packing of three adjacent molecules centered at 0, $\frac{1}{2}$, 0; $\frac{1}{2}$, $\frac{1}{2}$, 0 and 1, $\frac{1}{2}$, 0. Only the molecule in the center of this Figure is shown in Fig. 2.

of excess density. The double-atom refinement is related to the high-order technique, because the K-shell electrons are the only contributors at high values of $\sin \theta/\lambda$, but it allows simultaneous exploitation of all, rather than part of the data. Two sets of scattering factors for the valence shell were used, while the core scattering was left unmodified at the self-consistent-field value, as described by Stewart (1970).

In addition to the double set of positional parameters, the refinement includes as variables the scale factor, all temperature parameters and valence-shell occupancy factors, while the total number of electrons is constrained to keep the molecule neutral.

The positional and thermal parameters obtained with the two methods are listed in Table 3, while agreement factors are included in Table 2. The double-atom refinement gives an appreciable improvement in agreement in comparison with the conventional least-squares refinement, especially when Slater-type orbitals (STO) are used.

Net atomic charges (Table 6) are not significantly different from zero, which seems to contradict the large dipole moment commonly measured for cyano compounds. Ethyl cyanide, for example, has a dipole moment of 4D (Hurdis & Smyth, 1943), which for a bond of 1·16 Å length and a point charge approximation corresponds to a net charge of about 0·6 electrons on the carbon and nitrogen atoms.

Table 6. *Net atomic charges (electrons) as determined by double atom refinement*

Basis set	HF	STO	Calc INDO
N	0·20 (11)	−0·06 (11)	−0·15
C(2)	−0·28 (14)	−0·04 (12)	+0·12
C(1)	0·16 (15)	0·20 (14)	+0·07

Charges calculated for TCNE with the INDO method (Table 6,) are much smaller than 0·6 electron, but still not close to the experimental results, which, however, have large standard deviations. It is interesting that the discrepancy between the core and valence shell positions, discussed below, predicts a dipole moment with the positive pole towards the nitrogen.

Positional parameters obtained with Hartree–Fock (HF) and STO basis-sets are very similar. Both sets predict a discrepancy between the positions of the nitrogen core and its valence shell, the latter being displaced by about 0·05 Å relative to the all-data position, towards the center of the triple bond. As expected, the core position undergoes a small compensating shift and its parameters agree quite well with the results of the high-order refinement.

The high-order refinement gives indication of a small shift of C(2), the high-order position of this atom being further away from the center of the triple bond than the result obtained with all data. But the discrepancy is small and not confirmed outside the confidence limits by the double-atom method.

To apply the correction for thermal motion to the bond lengths the physically reasonable assumption has been made that the nitrogen atom rides on C(2), and C(2) rides on C(1). The Gaussian width parameters (q^2) has been taken as infinite; thus the true correction might be slightly smaller.

Compared with the full-data results the change in the C≡N bond length is appreciable (Table 5) and indeed, after correction for thermal motion a value is obtained which agrees very well with the electron diffraction results.

Though some accurate spectroscopic values on C≡N bond lengths are available, comparison is complicated by possible differences in bond order. The closest analogue to TCNE among the molecules studied is vinyl cyanide (Costain & Stoicheff, 1959), in which the C≡N distance is 1·164 (1) Å.* It is encouraging that this value is also close to the results obtained with the high-order and double-atom methods.

We conclude that the high-order and double-atom refinement methods can yield more reliable bond lengths when atoms with an aspherical charge density are involved.

Finally, the high-order temperature factors are generally lower than those obtained with the full data set (Table 3) as expected from comparison of X-ray and neutron diffraction data (Coppens, 1968). The difference is not reproduced with the double-atom method when HF scattering factors are employed, but STO valence shell form factors give better agreement with the high-order refinement for this structure. This and the lower R values obtained with STO form factors indicate that optimized Slater-type orbitals give a better fit to the valence shell density that the isolated-atom HF wave functions.

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* INDO calculations confirm that the C≡N bond orders in TCNE and vinyl cyanide are practically equal.

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Structural Studies of Metal Dithiocarbamates. V. The Crystal and Molecular Structure of Bis-(*N*,*N*-Diethyldithiocarbamato)tellurium(II)*

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Tellurium(II) bis-(*N*,*N*-diethyldithiocarbamate), [Te(S_2CNEt_2)$_2$], forms red monoclinic crystals, a = 15·191, b = 8·425, c = 14·841 Å, β = 117·66°, space group $P2_1/c$, with four formula units in the unit cell. The structure has been solved by standard methods and refined by block-diagonal matrix least-squares methods, using 2012 photographic observations, to a final R value of 0·081. The four sulphur atoms in the molecule are bound to tellurium with two short bonds [average 2·519 (3) Å] and two long ones [2·830 (3) and 2·893 (4) Å]. A fifth sulphur atom, belonging to the centrosymmetrically related molecule, approaches tellurium at a distance of 3·579 (5) Å. Tellurium and the five sulphur atoms lie approximately in a plane. Rationalization of the coordination around the tellurium atom is attempted on the basis of both the three-centre bond and the full hybridization theories.

For many of the heavier non-transition elements, the presence of low-lying *d* orbitals means that the number of electron pairs in the valence shell may exceed four. Thus the stereochemistry and bonding in compounds of these elements are varied and often complex, especially when the ligands can form chelates with the metal. Moreover the presence of one or more lone pairs in the valence shell of the metal makes rationalization of the shape of the molecule more difficult.

As part of the current studies of this Laboratory on metal dithiocarbamates, we investigated the structure of tellurium(II) (*N*,*N*-diethyldithiocarbamate), in which tellurium has low-lying *d* orbitals and two lone pairs in its valence shell, in order to contribute to the understanding of the stereochemistry of these compounds.

Experimental

(with technical assistance from Mr P. MURA)

Crystal data

Tellurium(II) bis-(*N*,*N*-diethyldithiocarbamate), [Te(S_2CNEt_2)$_2$], was synthesized as described in the literature (Foss & Pitha, 1953). Red crystals suitable for single-crystal X-ray analysis were grown from carbon disulphide–ether solutions; they are stable in air and to X-rays.

Preliminary X-ray and optical examinations of the crystals indicated that they belong to the monoclinic system. The space group, $P2_1/c$ (No. 14), was assigned on the basis of the systematic absences ($h0l$, $l=2n+1$; $0k0$, $k=2n+1$).

Unit-cell dimensions at about 23 °C are: $a = 15{\cdot}191 \pm 0{\cdot}002$, $b = 8{\cdot}425 \pm 0{\cdot}002$, $c = 14{\cdot}841 \pm 0{\cdot}002$ Å, $\beta = 117{\cdot}66 \pm 0{\cdot}02°$; these were determined by a least-squares refinement of seventy 2θ values measured on $hk0$ and $h0l$ Weissenberg photographs calibrated with superimposed ZnO powder lines, using Cu $K\alpha$ radiation (λ = 1·5418 Å). The measured density (by flotation in a $ZnCl_2$ solution) of 1·68 ± 0·01 g.cm^{-3} agrees well with the value of 1·670 g.cm^{-3} calculated for four [Te(S_2CNEt_2)$_2$] units of formula weight 424·14 in the cell of volume 1687·31 Å^3.

The X-ray intensities were estimated visually from sets of multiple-film equi-inclination Weissenberg photographs taken at room-temperature about the b (8 layers, $h0l$ to $h7l$) and c (5 layers $hk0$ to $hk4$) axes, with Ni-filtered Cu $K\alpha$ radiation, using two different crystals. They were both well formed, with the following forms developed: {100}, {001}, {10$\bar{1}$}, {011}, {110} and {11$\bar{1}$}. The approximate dimensions of the crystals were 0·20 × 0·20 × 0·25 and 0·20 × 0·25 × 0·50 mm respcctivcly.

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* Part IV: *J. Chem. Soc.* (*A*) (1968) p. 1351. Preliminary results on the structure of other metal dithiocarbamates not yet described in this series have been published in *Chem. Commun.* (1966) p. 476; (1967) p. 583; (1968) p. 302; (1968) p. 572; (1970) p. 743.

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