

Crystal Structure Investigations of Dihalofumaronitriles.

I. Dichlorofumaronitrile

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Dichlorofumaronitrile crystallizes in the monoclinic space group $C2/c$ with cell dimensions $a = 7.89_5$ Å; $b = 9.91_2$ Å; $c = 7.66_3$ Å; $\beta = 98.4^\circ$. The crystal structure has been determined with the use of 1010 reflections collected on a four-circle diffractometer ($MoK\alpha$ radiation).

The influence of the asymmetric distribution of bonding electrons on the bond length values obtained has been demonstrated. In the final refinement only the 700 reflections with $\sin \theta/\lambda > 0.5$ Å⁻¹ were applied in order to reduce this effect; the final weighted R -factor was 0.028.

The molecules are situated at centres of symmetry $(\frac{1}{2}, \frac{1}{2}, 0)$; the bond lengths were: C=C 1.35₀ Å; C-C 1.42₇ Å; C-Cl 1.70₂ Å; C≡N 1.14₇ Å.

Crystal structure examinations of dihalofumaronitriles have been undertaken at this laboratory. The cyano nitrogen may be expected to act as a weak electron donor in a charge-transfer bond to a halogen atom of a neighbouring molecule, at least for the iodine and the bromine compounds. Such bonds have been shown to exist in the cyanogen- and the cyanoacetylene halides.^{1,2} Spectroscopic investigations of dihalofumaronitriles have previously been carried out at this university.³

EXPERIMENTAL

The sample of dichlorofumaronitrile originated from Dr. L. Russel and was given to us by Dr. P. Klæboe.³ Crystals obtained by sublimation were well suited for the X-ray experiments.

Unit cell parameters were determined by least-squares methods from diffractometer measurements of 35 reflections.

Absent reflections are (hkl) for $h+l=2n+1$, and $(h0l)$ for $l=2n+1$. Possible space groups are thus Cc or $C2/c$, of which the latter turned out to be the correct one.

Three-dimensional intensity data were recorded with the use of an automatic Picker diffractometer with graphite crystal monochromated $MoK\alpha$ radiation. Because of the volatility of the substance the crystal was kept in a sealed-off capillary tube (Pyrex, wall thickness less than 0.01 mm) during the experiments. The crystal used for the data col-

lection had dimensions $0.25 \times 0.35 \times 0.52$ mm³ and was mounted with the direction $\mathbf{b}^* + 2\mathbf{c}^*$ along the φ -axis. The $\omega - 2\theta$ scanning mode was used, the 2θ scan speed being 1° min^{-1} through the scan range of 0.8° below $2\theta(\alpha_1)$ to 0.8° above $2\theta(\alpha_2)$. Background counts were taken for 25 sec at each of the scan range limits.

The intensities of three standard reflections measured for every 100 reflections of the data set showed a variation of less than 2 % during the collection of data. The standard deviations of the intensities were estimated to be the square root of the total counts with a 2 % addition for the instability.

Out of the 1309 unique reflections with $\sin \theta/\lambda$ less than 0.8 \AA^{-1} , 1010 had net intensities larger than twice the standard deviation. These were regarded as observed whereas the remaining reflections were excluded from the calculations. The ratio of the number of observed reflections to the number of parameters refined (37) was 27.

Corrections were made for Lorentz, polarization, and absorption effects. The transmission factor varied between 0.70 and 0.81. Atomic form factors were those of Hanson *et al.*⁴

Computer programs applied during the investigation are described in Ref. 5.

CRYSTAL DATA

Dichlorofumaronitrile, $\text{C}_4\text{N}_2\text{Cl}_2$, m.p. $58.5 - 59.5^\circ\text{C}$,³ monoclinic; $a = 7.8950(12) \text{ \AA}$, $b = 9.9115(12) \text{ \AA}$, $c = 7.6630(13) \text{ \AA}$, $\beta = 98.47(1)^\circ$. Figures in parentheses are estimated standard deviations. $V = 593.1 \text{ \AA}^3$, $M = 146.9$, $F(000) = 288$, $\mu = 0.968 \text{ mm}^{-1}$, $Z = 4$, $\rho_{\text{calc}} = 1.645 \text{ g cm}^{-3}$. Space group $C2/c$.

STRUCTURE DETERMINATION

The structure was solved by the heavy atom Patterson method. Least squares refinements using isotropic thermal parameters resulted in an R_w of 0.14; introduction of anisotropic thermal parameters in the further refinement brought the R_w -value for the 1010 reflections down to 0.039 ($R = 0.064$). No secondary extinction effects were observed. However, bond distances calculated on the basis of these parameters seemed unreasonable. The overdetermination ratio (27.2) was higher than usual in most structure determination of organic compounds. Exclusion of the low angle data was therefore found justified in order to avoid effects from an asymmetric valence electron distribution without reducing the accuracy significantly.

Successive least-squares refinements with increasing inner cut-off limits in $\sin \theta/\lambda$ for the applied intensity data were carried out. A minimum in the R_w -value was found using the data above $\sin \theta/\lambda$ equal to 0.5 \AA^{-1} (700 reflections). According to Allmann⁶ the contribution to the atomic form factor from the bonding electrons is very small for $\sin \theta/\lambda$ values larger than this limit. Refinements using the data within the copper sphere yielded essentially the same structural parameters as when all the data were applied. A summary of the calculations is given in Table 1.

The positional and thermal parameters resulting from the refinement including the 700 intensities outside $\sin \theta/\lambda = 0.5 \text{ \AA}^{-1}$ may be found in Table 2. Corresponding structure factor data are listed in Table 3.

An analysis of the atomic thermal motions is presented in Table 4. Rigid-body calculations yielded a negative eigenvalue of \mathbf{L} , probably because the atoms are situated close to a quadratic curve.⁷

Table 1. Intramolecular distances (Å) as found when various parts of the experimental data were employed in the least-squares refinements.^a

Data	R ₁ %	R ₂ %	R _w %	N	N/P	C1-C1	C1-C2	C2-N	C1-C1'
sin $\theta/\lambda < 0.64$	6.65	5.73	3.72	608	16.4	1.714(3)	1.444(4)	1.128(3)	1.310(5)
All data	6.40	6.40	3.89	1010	27.2	1.713(2)	1.443(3)	1.128(3)	1.312(4)
sin $\theta/\lambda > 0.35$	6.40	6.74	3.58	903	24.4	1.704(2)	1.433(3)	1.140(3)	1.341(4)
sin $\theta/\lambda > 0.44$	6.30	6.28	3.09	796	21.5	1.702(2)	1.433(3)	1.138(4)	1.348(4)
sin $\theta/\lambda > 0.50$	6.59	6.06	2.77	700	18.9	1.702(2)	1.427(3)	1.147(4)	1.350(4)
sin $\theta/\lambda > 0.55$	6.79	6.57	2.88	610	16.5	1.704(2)	1.426(3)	1.152(4)	1.346(4)
sin $\theta/\lambda > 0.59$	6.97	6.84	2.84	514	13.9	1.704(2)	1.424(3)	1.151(4)	1.346(4)
sin $\theta/\lambda > 0.64$	7.24	7.36	3.08	402	10.9	1.707(3)	1.432(4)	1.151(4)	1.327(5)

^a R₁ and R₂ include all data and data used in the refinement, respectively. N denotes the number of data in the refinement procedure and N/P is the overdetermination ratio. Estimated standard deviations (in parentheses) apply to the least significant digits. \downarrow

Table 2. Fractional atomic coordinates and thermal parameters with estimated standard deviations ($\times 10^5$). The temperature factor is given by $\exp-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)$.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	B ₁₁	B ₂₂	B ₃₃	B ₁₂	B ₁₃	B ₂₃
Cl	-1057	19663	790	1596	1244	2860	-613	775	-391
	7	7	10	13	9	18	10	12	13
N	19926	50491	19358	2649	1190	3096	1	940	-1239
	43	31	50	46	24	55	55	78	63
C1	18178	27729	3065	1603	832	1705	-207	362	-33
	23	18	25	23	14	28	28	37	29
C2	19471	40468	11823	2114	933	1981	31	582	-315
	32	24	32	34	18	34	36	52	39

Bond distances and angles corresponding to the parameters of Table 2 are given in Fig. 1. Standard deviations were calculated from the correlation matrix. The crystal structure as viewed along *c* is illustrated in Fig. 2.

DISCUSSION

The effect of the asymmetry in the valence electron distribution is clearly demonstrated in Table 1. The double and triple bond length values show a marked increase when successive larger parts of the low angle data are omitted from the refinement. The shifts are 0.038 Å and 0.019 Å, respectively, when the results from all data are compared with those of the data above $\sin \theta/\lambda = 0.5 \text{ \AA}^{-1}$. A similar and an alternative procedure for eliminating the effect from the valence electrons have recently been applied in the structure determination of cubic tetracyanoethylene.⁸ The larger shift for the double bond in the present investigation may partly be due to systematic errors in the low angle data affecting specially the electron density close to centres of symmetry.

Table 3. Continued.

Table with multiple columns of numerical data, organized in groups of four columns each. Each group starts with a header row of small integers (e.g., 4 8 4 112 - 116) followed by a grid of values separated by spaces and dashes.

Table 4. R.m.s. amplitudes of vibration $(\bar{u}^2)^{\frac{1}{2}}(\text{\AA})$ and B values (\AA^2) along the principal axes of vibration given by the components of a unit vector e in fractional coordinates ($\times 10^3$).

Atom	$(\bar{u}^2)^{\frac{1}{2}}$	B	e_x	e_y	e_z
Cl	.293	6.77	28	-33	124
	.257	5.22	-59	80	43
	.205	3.32	110	52	14
	.321	8.12	11	-48	116
N	.286	6.45	128	7	11
	.215	3.64	-4	88	62
	.229	4.15	-96	28	64
	.221	3.86	68	-29	114
C1	.199	3.13	50	93	17
	.256	5.17	125	9	-5
	.245	4.75	26	-39	121
C2	.209	3.45	-1	92	52

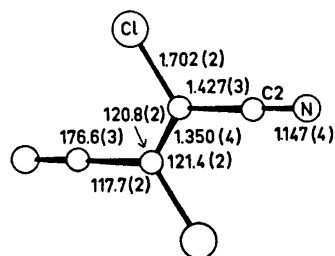


Fig. 1. Bond distances (\AA) and angles ($^\circ$) in dichlorofumaronitrile.

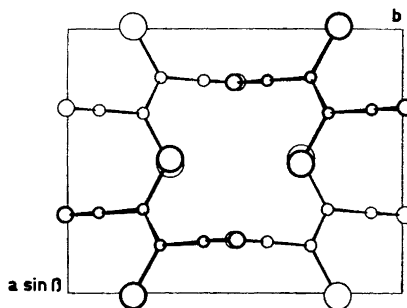


Fig. 2. The molecular packing as viewed along the c axis.

Riding corrections of bond lengths from the final parameter set ($\sin \theta/\lambda > 0.5$) resulted in C-Cl 1.720 \AA , C-C 1.437 \AA , and C \equiv N 1.179 \AA . The corrections, especially in the cyano bond, seem too large, and a curvilinear component should have been taken into account. In the following, bond length values not corrected for thermal motion are discussed.

The C–C double bond length of 1.350 Å is not significantly different from the value found in tetracyanoethylene (1.353 Å in the cubic form⁸ and 1.357 Å in the gas phase⁹) and in tetrachloroethylene (1.354 Å, gas phase¹⁰).

In a study of carbon–chlorine bonds in aromatic systems Rudman¹¹ reports C–Cl bond lengths found in the literature ranging from 1.70 Å to 1.76 Å. Our result, 1.702 Å, is slightly (0.016 Å) shorter than that found for tetrachloroethylene.¹⁰

The C–C single bond, the C–N triple bond as well as the bond angles are essentially the same as those determined in tetracyanoethylene.^{8,9}

The molecule shows only slight deviations from a planar model, the largest distance from the least-squares plane being 0.017 Å (C2). If the nitrogen atoms are omitted from the calculations, the rest of the atoms are found to be coplanar. The main axis of the atomic thermal vibration for the terminal atoms are approximately normal to the molecular plane.

The packing in the crystal is shown in Fig. 2. No *inter*-molecular contacts shorter than corresponding sums of van der Waals radii are observed and consequently no charge-transfer bonds are present.

In order to examine the effect of the valence electrons more closely, X-ray investigations of salts of the isoelectronic divalent anion of the dimercapto-fumaronitrile will be carried out.

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