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The Crystal Structure of Cyanogen

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The structure of crystalline cyanogen, NCCN, has been determined at −95 °C by precession methods. The space group is *Pcab* and the lattice constants are $a = 6{\cdot}31$, $b = 7{\cdot}08$, $c = 6{\cdot}19$ Å. The four molecules per unit cell are so arranged that all of the nitrogen atoms lie in a hexagonal close packed array. This is a result of the fact that the intramolecular N–N distance closely approximates the van der Waals diameter for nitrogen.

Introduction

The linear structure of cyanogen, NCCN, has been described in detail by Pauling, Springall & Palmer (1939) from electron-diffraction studies of the gas. In addition, a number of infrared and Raman spectroscopic studies have been reported (Møller & Stoicheff, 1954). The present investigation was undertaken to provide a detailed description of the molecular arrangement and symmetry in the crystal to augment a solid state infrared study currently underway (Nixon, 1962). Of particular interest is the antisymmetric C–N stretching mode, ν_3, which is observed as two infrared active components separated by about two wave numbers rather than as the triplet which would be predicted upon the basis of symmetry. An interpretation of the correlation field splitting is being sought in terms of induced dipole-induced dipole interaction.

Experimental procedure

Cyanogen was prepared by pyrolysis of silver cyanide, purified and sealed in thin-walled glass capillaries. Although cyanogen melts at −34·4 °C and boils at −20·5 °C it was possible to cycle many of the filled capillaries through room temperature since the gas condenses at moderate pressures.

Crystals were grown *in situ*, on a precession camera, by driving the capillary into a jet of cold nitrogen gas by means of a clock motor coupled to the translation mechanism of the camera. The cooling system provided adequate temperature control down to −125 °C and operated over the full precession range of the camera.

Precession X-ray photographs were taken at -95 ± 2 °C, using both Cu $K\alpha$ and Mo $K\alpha$ radiation. Intensity measurements were made on accurately timed multiple exposures made from zero, first and second level photographs taken down [010], [100], and [110]. The intensities were estimated visually by comparison with a calibrated film strip of 26 reflections. Out of a total of 345 independent reflections in range with Mo $K\alpha$ radiation, 125 were of measurable intensity.

In growing crystals within a capillary *in situ* there exists the possibility of obtaining a crystal too long to be bathed completely in the X-ray beam. Owing to the nature of the precession motion, the volume of irradiated crystal will vary from reflection to reflection. Thus, for example, for a very long crystal inclined 30° to the spindle axis, and with $\bar{\mu} = 30°$, the intercepted volume can be as much as twice its value at normal incidence. The average values of the errors in relative intensities associated with this effect will, of course, be very much smaller. They will depend upon the distribution of the incidence angles for all reflections. However small they are, the errors will not be random, but rather will be systematically related to the orientation of the crystal with respect to the capillary axis.

Since every diffraction maximum is the superposition of two reflections occurring with the capillary in different positions, each intensity reading involves an averaging process. In addition, because of the symmetry, it was possible to record and measure most reflections four times. This introduced a further averaging process which, it was felt, reduced the systematic errors to negligible values. Nevertheless, because the crystal was indeed long compared with the diameter of the X-ray beam, appropriate corrections (Parkes & Hughes, 1963) were applied to individual reflections to provide a second set of data which appeared, superficially, to be only slightly different from the first.

Structure determination

Systematic absences among the observed reflections were consistent with the uniquely determinable space group *Pcab*, with the conventions that $b > a > c$. The orthorhombic cell constants were determined to be

$$a = 6{\cdot}31,\ b = 7{\cdot}08,\ c = 6{\cdot}19\ \text{Å},$$

with a standard deviation of 0·03 Å for each. This corresponds to a crystal density of 1·25 g.cm^{-3}.

It should be noted at this point that, at least on one occasion, a crystal, when warmed some thirty degrees, showed several weak reflections which were inconsistent with the existence of two of the glide planes. These reflections were invariant to subsequent recooling and to changes of orientation of the crystal. Although this phenomenon was not reproducible and did not occur in crystals grown at the higher temperature, it appears that a second polymorphic form exists for cyanogen.

A linear trial structure was characterized in terms of two orientation angles and values of R were calculated from 30 low angle reflections by iteratively varying these angles in 10° increments. At this point, with an R of 0·11, the structure was refined on an I.B.M. 7090 computer using the Gantzel, Sparks & Trueblood full matrix least-squares program as modified by Okaya (1962). A total of 125 observed data and 220 unobserved data (entered as $\frac{1}{2}F_{\mathrm{min.\,obs.}}$) were utilized with a weighting proportional to F^2 for all $F<6$ and constant for all $F \geq 6$. A second refinement was performed with all of the data corrected for variable crystal volume (Input Data II).

Since the intensity of the weakest spot on the calibrated film strip was significantly greater than the minimum observable, $F_{0\cdot5\ \mathrm{min.\,obs.}}$ was systematically greater than $F_{\mathrm{calc.}}$ for unobserved reflections. A least-squares analysis of refinement II indicated that it would be more appropriate to compare $F_{0\cdot35\ \mathrm{min.\,obs.}}$ with $F_{\mathrm{calc.}}$ Therefore a third refinement was run on data modified in this way (Input Data III).

Table 1

Input data	R (observed data only)	R (all data)
I	0·0911	0·2155
II	0·0870	0·2129
III	0·0865	0·2034

The results of these refinements are listed in Table 1, in which $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$. It can be seen that small but significant reductions in R were effected in going from refinements I to III. Of more interest, however, is the fact that the structure was affected. The uncorrected data I led to a deviation of 1° 40′ from linearity in NCCN with a standard deviation

Table 2. *Observed and calculated structure factors*

hkℓ	$\|F_o\|$	$\|F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$	hkℓ	$\|F_o\|$	$\|F_c\|$
002	25.9	-24.1	128	< 2.3	-0.8	206	7.3	-7.4	271	< 2.5	-1.5	401	17.4	-17.9	513	< 2.3	0.4	616	< 2.5	0.6
004	6.6	6.4	131	8.7	9.2	207	3.8	3.7	272	4.6	-4.0	402	10.4	10.3	514	3.6	-3.6	620	< 2.3	2.2
006	10.7	-11.6	132	< 1.6	-0.3	208	≤ 1.6	0.4	273	< 2.7	0.1	403	< 1.9	0.9	515	< 2.5	-3.0	621	< 2.3	-2.6
008	< 1.9	1.4	133	< 1.9	1.4	211	4.3	-4.6	274	< 2.8	-2.3	404	7.0	-7.1	516	< 2.5	0.5	622	< 2.5	0.6
012	11.0	-11.6	134	< 2.1	-2.3	212	6.3	-6.3	275	< 2.5	1.0	405	5.7	-5.3	517	< 2.5	-0.3	623	3.8	-4.1
014	< 1.9	0.3	135	6.8	-6.0	213	2.9	3.0	280	< 2.7	-1.6	406	< 2.1	-1.2	520	9.6	-8.4	624	< 2.7	-0.8
016	< 2.1	-1.5	136	< 2.5	1.1	214	< 2.1	-1.2	281	< 2.7	-1.9	407	3.9	3.3	521	7.6	6.1	625	< 2.8	-0.7
018	2.6	1.8	137	< 2.7	-0.4	215	< 2.3	-1.0	282	< 2.7	-2.5	411	3.4	-3.2	522	< 2.1	1.4	626	< 2.8	-0.7
020	29.9	26.8	138	< 2.5	-0.2	216	< 2.5	-0.3	283	< 2.8	3.3	412	< 1.9	-1.1	523	8.6	-6.9	640	< 2.5	5.0
022	9.8	8.8	140	< 1.6	-2.9	217	< 2.5	1.5	284	< 2.8	2.1	413	< 2.1	1.5	524	< 2.5	-0.2	641	< 2.5	-1.2
024	6.8	-6.3	141	5.4	-6.6	218	< 2.5	1.0	291	< 2.8	-0.4	414	< 2.3	-2.1	525	< 2.7	2.4	642	< 2.5	-2.9
026	4.4	-4.7	142	< 1.9	-1.3	220	17.3	17.7	292	< 2.8	-1.3	415	< 2.5	0.2	526	< 2.8	2.6	643	< 2.7	-1.0
028	< 1.6	-0.6	143	9.1	-9.9	221	2.6	-3.3	311	12.8	12.3	416	< 2.5	0.9	531	< 2.1	2.9	644	< 2.7	1.7
032	15.6	-14.4	144	< 2.3	1.0	222	8.0	6.3	312	9.2	-9.5	417	< 2.5	1.1	532	< 2.3	3.0	645	< 2.7	-0.3
034	4.8	-4.7	145	< 2.5	-1.7	223	5.3	-4.5	313	< 1.9	-0.9	420	8.6	7.2	533	< 2.3	-1.3	651	< 2.5	-3.6
036	< 2.1	0.1	146	< 2.5	1.0	224	5.0	-5.1	314	< 2.1	-2.3	421	3.8	-3.4	534	< 2.5	-2.3	652	< 2.5	-1.6
038	2.7	2.4	147	< 2.7	2.2	225	3.1	-0.8	315	5.3	-5.3	422	2.9	2.6	535	< 2.7	-0.5	653	< 2.5	0.5
040	15.7	-13.6	151	< 1.9	0.3	226	4.5	-3.8	316	< 2.5	-0.4	423	5.9	-5.4	536	< 2.7	0.7	654	< 2.5	-0.2
042	17.8	17.0	152	< 2.1	0.4	227	< 2.1	0.9	317	< 2.5	-1.7	424	< 2.3	-2.7	540	5.4	-5.4	660	< 2.1	0.1
044	7.6	-10.0	153	< 2.1	0.2	228	< 1.3	-0.3	318	< 2.5	1.9	425	< 2.5	-0.9	541	< 2.3	-1.8	661	< 2.7	0.3
046	3.1	2.0	154	< 2.3	-0.2	231	5.3	-5.6	320	26.3	-26.4	426	< 2.7	-2.1	542	< 2.3	-2.6	662	< 1.9	0.3
052	8.4	-7.7	155	< 2.5	-0.7	232	9.5	-9.9	321	3.5	-3.2	427	< 2.7	1.2	543	< 2.3	-2.4	663	< 1.6	1.0
054	7.2	-7.2	156	< 2.5	0.3	233	< 1.9	1.6	322	12.2	13.4	431	5.6	-5.6	544	< 2.5	2.5	711	< 2.5	0.5
056	3.1	2.3	157	< 2.5	0.2	234	< 5.2	-4.5	323	5.3	-5.4	432	4.2	-3.8	545	< 2.5	-0.4	712	< 2.5	-3.8
060	< 1.9	-1.5	160	2.7	2.5	235	< 2.3	1.1	324	6.4	-6.3	433	< 2.1	1.0	546	< 2.3	2.0	713	< 2.5	0.1
062	3.5	-1.4	161	2.7	2.4	236	< 2.5	0.5	325	< 2.3	-0.8	434	< 2.3	-3.1	551	< 2.1	0.8	714	< 2.5	-2.8
064	< 2.1	0.9	162	4.2	-4.1	237	< 2.5	1.4	326	6.3	5.1	435	< 2.5	2.4	552	< 2.1	0.0	715	< 2.5	-0.6
066	< 1.9	0.9	163	10.6	-10.9	238	< 3.0	1.8	327	< 2.5	-1.8	436	< 2.5	0.9	553	< 2.1	-0.4	720	< 2.5	-0.9
072	5.4	-4.6	164	< 2.5	2.8	240	2.9	-2.6	331	5.7	6.1	437	< 2.3	1.4	554	< 2.1	0.2	721	< 2.5	2.6
074	< 2.1	-2.9	165	< 2.5	1.4	241	12.3	11.9	332	< 1.9	-1.8	440	7.1	7.3	555	< 1.9	-0.2	722	< 2.7	-2.8
080	< 2.1	-0.2	166	< 2.5	-0.5	242	6.6	7.3	333	< 1.9	-1.0	441	5.0	5.7	560	< 2.5	-2.5	723	< 2.7	-2.1
082	5.5	-4.7	171	3.1	-2.4	243	9.1	-9.2	334	3.9	-3.8	442	3.1	-2.9	561	3.5	-4.2	724	< 2.8	2.3
084	4.0	3.6	172	< 2.5	0.3	244	4.5	-4.9	335	< 2.1	-2.7	443	5.5	-6.1	562	< 2.5	-2.7	751	< 2.7	0.5
092	< 1.9	-1.6	173	< 2.5	-0.6	245	4.2	3.9	336	< 2.1	1.7	444	< 2.1	1.2	563	< 2.5	0.2	752	< 2.7	-0.2
111	28.1	29.2	174	< 2.5	1.0	246	< 2.7	0.2	337	< 1.9	-1.1	445	< 2.1	2.4	564	< 2.5	2.5	800	< 2.1	-1.2
112	6.3	-6.2	175	< 2.7	2.4	247	< 2.7	-1.5	340	4.6	-5.7	446	< 1.9	-2.0	571	< 2.7	-0.7	801	< 2.1	0.1
113	4.9	-4.6	180	< 2.5	-0.6	251	2.6	-2.7	341	4.8	-4.0	451	3.8	-4.1	572	< 2.7	1.5	802	< 1.9	0.7
114	< 1.9	-0.5	181	< 2.5	-2.0	252	5.6	-6.9	342	3.6	-2.8	452	3.9	-4.5	573	< 2.7	0.5	803	3.2	-4.6
115	6.1	-6.0	182	< 2.5	-0.1	253	< 2.3	-1.1	343	6.3	-6.3	453	< 2.3	-0.3	600	2.2	-3.7	811	< 2.5	-0.8
116	< 2.1	-0.5	183	< 2.5	-2.3	254	4.8	-5.1	344	3.4	2.4	454	< 2.5	-1.8	601	3.4	-3.1	812	< 2.5	0.2
117	4.4	-3.6	184	< 2.7	0.2	255	4.6	3.1	345	< 2.5	-1.0	455	< 2.5	3.3	602	4.6	6.1	813	< 2.5	-0.2
118	< 1.6	0.9	191	< 2.7	-2.6	256	< 2.8	1.3	346	< 2.5	2.1	456	< 2.3	-0.0	603	4.7	-5.7	820	< 2.8	0.1
120	21.6	-22.9	192	< 2.7	0.6	257	< 3.0	-0.1	347	< 2.3	1.4	460	< 2.5	-0.4	604	4.1	-4.3	821	< 2.8	-1.5
121	33.5	-37.5	193	< 2.7	0.3	260	< 2.1	-1.1	351	< 2.1	0.7	461	< 2.5	0.3	605	< 2.1	-1.0	822	< 2.8	-0.1
122	11.2	12.3	200	47.3	46.7	261	< 2.1	0.3	352	< 2.3	0.5	462	< 2.5	-0.3	606	< 1.3	0.8	823	< 2.8	-2.3
123	6.8	6.9	201	37.6	-36.4	262	< 2.3	-1.1	353	< 2.3	-0.3	463	< 2.7	1.5	611	< 2.3	-1.6			
124	5.0	-5.2	202	4.7	-4.0	263	< 2.5	1.1	354	< 2.5	-0.2	464	< 2.7	0.3	612	< 2.3	0.1			
125	7.7	-8.0	203	9.7	9.8	264	< 2.7	0.7	355	< 2.7	-0.2	465	< 2.7	0.2	613	< 2.5	-0.0			
126	4.0	3.1	204	< 1.9	-0.9	265	< 2.8	0.3	356	< 2.7	0.3	511	3.2	3.6	614	< 2.5	-1.0			
127	5.0	4.1	205	7.1	-7.7	266	< 2.8	0.6	400	< 1.6	1.1	512	6.4	-6.5	615	< 2.5	1.2			

of only 18′. Refinements II and III led to structures in which NCCN deviated from linearity by only 22′ with the same 18′ standard deviation, that is, by an insignificant amount. This difference in structure is a result of the correction of systematic errors in the observed intensities because of variations in irradiated crystal volume. A comparison of the observed and calculated structure factors for the third set of data is shown in Table 2.

Discussion of the structure

The refined structure parameters, based on the third set of data, are listed in Table 3. Although anisotropic temperature factors were used, the least-squares refinement program did not require that all of the roots q_i of the determinant $|\mathbf{A}-q\mathbf{E}|=0$, where $-\ln T=\mathbf{X}'\mathbf{A}\mathbf{X}$, be positive, that is, that the matrix be positive definite. For both the carbon and the nitrogen, two of the roots were imaginary. However, since the principal terms did not differ significantly from their average, after being converted to reciprocal lattice coordinates, the temperature factor in each case is essentially isotropic. The equivalent B is included in Table 3. Since isotropic form factors were used, the temperature factors along the molecular axis undoubtedly include a component to allow for distortion of the atoms into the triple bond.

Table 3. *Refined structure parameters*

	Carbon	Nitrogen
x	$0{\cdot}0327 \pm 0{\cdot}0007$	$0{\cdot}0857 \pm 0{\cdot}0006$
y	$0{\cdot}0483 \pm 0{\cdot}0007$	$0{\cdot}1271 \pm 0{\cdot}0006$
z	$0{\cdot}0900 \pm 0{\cdot}0007$	$0{\cdot}2386 \pm 0{\cdot}0009$
α	$0{\cdot}018 \pm 0{\cdot}001$	$0{\cdot}027 \pm 0{\cdot}001$
β	$0{\cdot}015 \pm 0{\cdot}001$	$0{\cdot}021 \pm 0{\cdot}001$
γ	$0{\cdot}022 \pm 0{\cdot}001$	$0{\cdot}027 \pm 0{\cdot}001$
δ	$0{\cdot}005 \pm 0{\cdot}002$	$-0{\cdot}003 \pm 0{\cdot}002$
ε	$-0{\cdot}000 \pm 0{\cdot}003$	$-0{\cdot}003 \pm 0{\cdot}003$
η	$-0{\cdot}001 \pm 0{\cdot}002$	$-0{\cdot}007 \pm 0{\cdot}002$
B	$3{\cdot}08$	$4{\cdot}22$

Least squares bond parameters

C−C	$1{\cdot}371 \pm 0{\cdot}009$
C≡N	$1{\cdot}127 \pm 0{\cdot}006$
C−C≡N	179° 38′ ± 18′

Final bond parameters

C−C	$1{\cdot}37 \pm 0{\cdot}02$ Å
C≡N	$1{\cdot}13 \pm 0{\cdot}015$ Å
C−C≡N	179° 38′ ± 18′

In spherical coordinates, the molecular axis lies along the line $\theta=59{\cdot}0°$, $\varphi=35{\cdot}4°$, with respect to the cell axes. The molecular and intermolecular configurations are such that the nitrogen atoms lie in a slightly distorted hexagonal closest packed arrangement; the pseudothreefold is parallel to c. This is possible because of the unique circumstance that in this molecule the nitrogen–nitrogen distance is essentially equal to the van der Waals diameter of nitrogen. The intramolecular nitrogen–nitrogen distance is 3·62 Å; intermolecular distances range from 3·54 to 3·86 Å. The packing arrangement is shown in Fig. 1, projections along a and c. The hexagonal array in a plane is accentuated by shading.

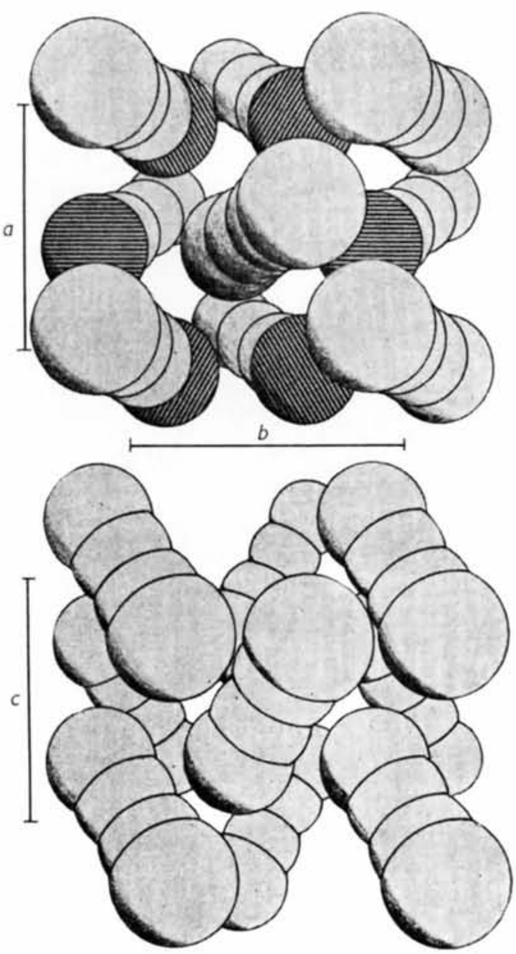

Fig. 1. Projection of cyanogen along [001] and [100].

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