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Z. V. ZVONKOVA, V. Ya. KRIVNOV, A. N. KHVATKINA

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Abstract

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Z. V. ZVONKOVA, V. Ya. KRIVNOV, A. N. KHVATKINA

NEW DETERMINATION OF THE ATOMIC AND ELECTRONIC STRUCTURE OF DICYANDIAMIDE

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Previously we determined the crystal structure of cyanamide, $N \equiv C—NH_2$ (^{1}). In the present work we give the results of an X-ray structural investigation of its dimer—dicyandiamide (see Table 1)—and of a quantum-chemical calculation of bond orders and atomic charges in the monomer and dimer.

Table 1

Formula	a	b	c	β	Fedorov group	Number of molecules in the cell	σ_x	σ_{pycn}
$C_2H_4N_4$	15.00	4.44	13.12	115°20′	$C_{2h}^6—C_{2/c}$	8	1.405	1.404

The crystal structure of dicyandiamide had been solved in an earlier work (^{2}) from one projection of the electron density $\rho(xz)$. The y coordinates of the atoms were determined by trial. We have refined the structure of dicyandiamide by means of three-dimensional syntheses of the electron density. Using CuK_α radiation, 479 reflections hkl were obtained. The atomic coordinates from work (^{2}) were taken as the starting coordinates. Calculations of the electron density were performed on the "Kristall" machine and the signs of the structural amplitudes on the "Minsk-1" machine. After nine successive approximations of the three-dimensional electron density of the crystal, the atomic coordinates listed in Table 2 were obtained together with the initial data. As was to be expected, the largest discrepancies were obtained in the y coordinates of the atoms. The discrepancy coefficient $R = 0.13$.

Table 2

Atoms	x^*	y^*	z^*	x^{**}	y^{**}	z^{**}
C_1	0.1310	0.1113	0.9292	0.1285	0.103	0.9275
C_2	0.1170	0.1717	0.0932	0.1145	0.171	0.0935
N_3	0.1651	0.9867	0.8736	0.1635	0.963	0.8735
N_4	0.0909	0.2488	0.9858	0.0920	0.251	0.9850

Atoms	x^*	y^*	z^*	x^{**}	y^{**}	z^{**}
N_5	0.1834	0.9600	0.1472	0.1795	0.939	0.1439
N_6	0.0729	0.3088	0.1477	0.0705	0.334	0.1450

* Our data. ** Data from work (2).

The interatomic distances and valence angles in the dicyandiamide molecule are given in Table 3.

In dicyandiamide the length of the $N_3 \equiv C_1$ bond is increased, while the length of the C_1—C_4 bond is decreased in comparison with cyanamide, where the interatomic distances are, according to X-ray structural data, respectively 1.15 and 1.31 Å (1), and according to infrared spectra, 1.17 and 1.32 Å (3). The frequency of the valence vibration of the $N \equiv C$ bond in cyanamide is close to the value for a nitrile group and is equal to 2,232 cm^{-1} (3) or 2,260 cm^{-1} (4). In dicyandiamide this frequency is lowered to 2,175 cm^{-1} (5), in agreement with the increase in the interatomic distance. The intermolecular distances $N_3 \dots N_5$ 2.98 Å and $N_4 \dots N_6$ 3.05 Å, $N_3 \dots N_6$ 3.11 Å indicate a weak hydrogen bond.

Table 3

	Distances, Å		Valence angles			
	our data	data (2)	x and z of work (2) and y of this work		our data	data (2)
C_1—N_3	1.19_2	1.22	1.18	N_3—C_1—N_4	180°	180°
C_1—N_4	1.29_2	1.28	1.26	C_1—N_4—C_2	119°	120°
C_2—N_4	1.33_5	1.36	1.36	N_4—C_2—N_5	124°	120°
C_2—N_5	1.33_2	1.37	1.31	N_4—C_2—N_6	118°	116°
C_2—N_6	1.31_3	1.34	1.29	N_5—C_2—N_6	118°	124°

Molecular diagrams of dicyandiamide and cyanamide.

A quantum-chemical calculation of the dicyandiamide molecule was carried out by the self-consistent-field MO LCAO method (in the π-electron approximation). The calculation was performed on a machine by means of iterations (6). The iterations were continued until $|g_n - g_{n-1}| < 10^{-4}$ and $|P_n - P_{n-1}| < 10^{-4}$, where g_n are the atomic charges and P_n the bond orders after the corresponding iteration. The values of the Coulomb and exchange integrals were taken as follows: $\alpha_3 = \alpha + 1.3\beta$, $\alpha_1 = \alpha_2 = \alpha_6 = \alpha + \beta$, $\alpha_4 = \alpha_5 = \alpha + 0.8\beta$, $\beta_{13} = 1.3\beta$, $\beta_{14} = \beta_{24} = 1.2\beta$, $\beta_{25} = \beta_{46} = \beta$ ($\alpha = 0$ and $\beta = -20$ kcal/mol). As a result, the charges on the atoms and the bond orders were calculated. The calculation was carried out under the assumption that the free electron pair of the nitrogen atom may either participate or not participate in the bond. Accordingly, for the different imino and amino forms of the dicyandiamide molecule, the wave functions of nitrogen atoms N_4 and N_5 were constructed a) with p_z-orbitals and b) without p_z-orbitals. The calculated molecular diagrams are given below; they indicate the orders of the π- and σ-bonds and the atomic charges.

imino (a) imino (b)

(Figure: molecular diagrams of dicyandiamide, imino forms)

amino (a) amino (b)

(Figure: molecular diagrams of dicyandiamide, amino forms)

The molecular diagram of cyanamide was calculated by the same method

$$\begin{array}{ccc} -0.19 & +0.07 & +0.12 \\ N_2 & C_1 & N_3 \\ & \underset{1.36}{\rule{2em}{0.4pt}} & \underset{2.93}{\equiv} \end{array}$$

The values of the Coulomb and exchange integrals were: $\alpha_1 = \alpha_3 = \alpha$, $\alpha_2 = \alpha + 0.2\beta$, $\beta_{1,3} = 1.4\beta$, $\beta_{1,2} = 1.2\beta$.

In dicyandiamide the order of the $N_3 \equiv C_1$ bond is smaller and the order of the C_1—N_4 bond is greater than in cyanamide. This is consistent with the change in the experimental interatomic distances in these molecules.

Discussion of the results of the work

To compare the results of the theoretical calculation with experimental data, use was made of the curve of the dependence between the order and length of C—N bonds, constructed with allowance for s—p hybridization of the carbon atom (^{7}). Table 4 gives the theoretical and experimental interatomic dis-

distances in angstroms in the dicyandiamide molecule. Our experimental data agree better with the calculated data. The literature experimental (^{2}) and calculated (^{8}) data show poorer agreement both with each other and with our data. The calculations of the dicyandiamide molecule in (^{8}) were performed without iterations. According to our experimental and calculated data (for the imino and amino forms), the lengths of all three bonds ($\mathrm{C_2 - N_4}$, $\mathrm{C_2 - N_5}$, and $\mathrm{C_2 - N_6}$) of the guanidine group are almost identical and lie in the narrow interval 1.32 ± 0.02 Å. It should be noted that the theoretical calculation of bond orders by the molecular-orbital method agrees well with the experimental data. In dicyandiamide and cyanamide, the largest discrepancies between the calculated and experimental lengths of the $\mathrm{C - N}$ bonds do not exceed 0.02 Å.

A crystal-chemical study of the nature of the chemical bond in structures with

$$\mathrm{S = C - N}$$

groups (9–11) established that, as the lengths of the $S = C$ bonds decrease, the lengths of the $C{-}N$ bonds also decrease. However, the length of the $S = C$ bond, equal to 1.5609 Å in the isothiocyanate group $S = C = N$, changes scarcely at all in the molecules $S = C = S$, $S = C = O$, and, consequently, does not depend on the nature of the other atoms S, N, and O attached to the thiocarbonyl group $S = C$. An important crystal-chemical discovery is that the lengths of the $S = C$ and $C - N$ bonds decrease as the valence angle of the carbon atom increases in the groups $S = C - N$, $N - C = C$, $S = C - C = C$. This is evident from the data in Table 5.

Figure 1 shows the general dependence of the interatomic distances $S = C$ (a) and $C - N$ (b) on the valence angle of the C atom. The values of the lengths of single bonds (points 9) show the maximum possible elongations of the $S - C$ and $C - N$ bonds. This regularity is due to the fact that bond orders increase with increasing participation of the lone pairs of electrons of the S, N, and O atoms in the chemical bond as the valence angle of the carbon atom increases. Its manifestation in the amide group

$$> N - C = O$$

is hindered by de—

Table 4

Bonds	Sum of covalent radii (imino)	Calculated distances: data (8), imino	Calculated distances: data (8), amino	Calculated distances: our data, imino, a	Calculated distances: our data, imino, b	Calculated distances: our data, amino, a	Calculated distances: our data, amino, b	Experimental distances
$C_1 - N_3$	1.15_5	1.19	1.19	1.17	1.17	1.16	1.16	1.19_2
$C_1 - N_4$	1.43	1.23	1.21	1.29	1.31_5	1.29	1.31_5	1.29_2
$C_2 - N_4$	1.45	1.32	1.31	1.33	1.33_5	1.34_5	1.32	1.33_5
$C_2 - N_5$	1.45	1.36	1.32_5	1.30_5	1.31_5	1.30_5	1.31	1.33_2
$C_2 - N_6$	1.25	1.32	1.32_5	1.31	1.31	1.30_5	1.31	1.31_3

Table 5

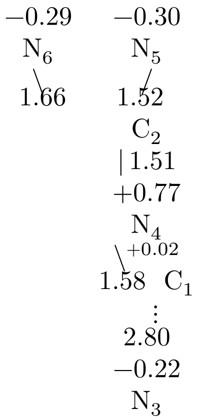
No.	Group	Valence angle, deg.	Bond length, Å: S = C	Bond length, Å: C − N	Compound
1	S = C = N	180	1.5609	1.2158	Isothiocyanate group (12)
2	S = C − N	136	1.60	1.29	Benzothiazoline-2-thione (10)
3	N − C = C	130	–	1.309	N-propylene-substituted rhodanine (13)
4	S = C − C = C	128.1	1.627	–	Dithiocyclopentene-3-thione (14)
5	S = C − N	128	1.63	1.35	Mercocyanine (15)
6	N − C = C	125	–	1.35	Mercocyanine (15)
7	S = C − N	124.2	1.64	1.37	Rhodanine (16)
8	S = C − N	124°	1.654	1.384	N-propylene-substituted rhodanine (13)
9	S—C—N	109.5	1.81	1.47	Single bonds

localization of the electron of the nitrogen atom, leading to a decrease in the length of the C—N bond and an increase in the length of the C=O bond according to the scheme $N^{+\delta} = C—O^{-\delta}$ (9). In dicyandiamide there is also considerable delocalization of the electrons of the nitrogen atoms. As a result, the C—N bond lengths in the molecule are substantially equalized in comparison with the sum of the covalent radii of the carbon and nitrogen atoms.

(Figure: Fig. 1)

Fig. 1

In the dicyandiamide molecule the valence angle N_3—C_1—N_4 considerably exceeds the valence angle N_4—C_2—N_5. Consequently, a calculation was carried out for the imino form of dicyandiamide with nitrogen atoms in different valence states: N_4 (with a p_z-orbital) and N_5 (without a p_z-orbital).



The positions of the hydrogen atoms will be established in a subsequent study.

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named after L. Ya. Karpov

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Note: Figure translations are in progress. See original paper for figures.