Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1964

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Vol. 155, No. 6

PHYSICAL CHEMISTRY

N. V. RANNEV, R. P. OZEROV

NEUTRON-DIFFRACTION DETERMINATION OF THE POSITION OF HYDROGEN ATOMS IN THE STRUCTURE OF DICYANDIAMIDE

(Presented by Academician N. V. Belov, 13 XII 1963)

The crystal and molecular structures of cyanamide dimer have been studied in detail by X-ray diffraction by Hughes ([1]), Z. V. Zvonkova, V. Ya. Krivnov, and A. N. Khvatkina ([2]), and also by means of optical spectra by B. I. Sukhorukov and A. I. Finkelshtein, Johnson, and Orville-Thomas ([3]). According to the X-ray data, this compound crystallizes in the monoclinic system, $a = 15.00$, $b = 4.44$, $c = 13.12$ Å, $\beta = 115°20'$, $z = 8$, space group C_{2h}^6—C^2/c. All atoms occupy general positions–8 (f), characterized by three parameters x, y, and z. The position of the hydrogen atoms, however, remained undetermined. In connection with this, until now there remained uncertainty in the choice of the chemical (structural) formula of the molecule:

$$\begin{matrix} & & \mathrm{H_2N} & & \\ \mathrm{C} & = & \mathrm{N} & - & \mathrm{C} \equiv \mathrm{N} \\ & & \mathrm{H_2N} & & \end{matrix} \qquad \text{(I)} \qquad \text{amino-} \tag{4}$$

$$\begin{matrix} & & \mathrm{H_2N} & & \\ \mathrm{C} & - & \mathrm{NH} & - & \mathrm{C} \equiv \mathrm{N} \\ & & \mathrm{HN} & & \end{matrix} \qquad \text{(II)} \qquad \text{imino-} \tag{5}$$

$$\begin{matrix} & & \mathrm{H_2N} & & \\ \mathrm{C} & - & \mathrm{N} & = & \mathrm{C} = \mathrm{NH} \\ & & \mathrm{HN} & & \end{matrix} \qquad \text{(III)} \tag{6,7}$$

The model of hydrogen bonds proposed by Hughes (on the basis of an analysis of interatomic distances) is compatible with all the formulae given. In papers ([3]) the conclusion is drawn that the molecule of dicyandiamide has the amino

Fig. 1. Projection of nuclear density along the *oy* axis—$\rho(xz)$

Figure 1: Fig. 1. Projection of nuclear density along the *oy* axis—$\rho(xz)$

form (formula I); nevertheless, theoretical calculations of the structure ([2,8]) cast doubt on the relative unambiguity of this proposal.

The purpose of the present work was to localize the hydrogen atoms by means of neutron diffraction, on the basis of which it would be possible to make an unambiguous choice of the correct structural formula of the compound.

Fig. 1. Projection of nuclear density along the *oy* axis—$\rho(xz)$

The investigation was carried out on the neutron-diffraction apparatus of the L. Ya. Karpov Institute of Physical Chemistry ([9]). The dicyandiamide crystal was a transparent prism of dimensions $14 \times 2.5 \times 2$ mm^3. From the crystal, 193 reflections of the type $h0l$ were obtained (within $\sin\theta/\lambda = 0.83$, $\lambda = 1.06$ Å), of which 119 were nonzero (the zero reflections correspond mainly to the periphery of the sphere of reflection).

Verification of the extinction law confirmed the indicated space group. Reflections of high intensity were recorded on an EPP-09 self-recording instrument; weak reflections were registered point by point. The intensity was converted to structure amplitudes in the usual way. No absorption corrections were introduced.

Preliminary calculations of the signs of the structure amplitudes were carried out

according to the coordinates of the nitrogen and carbon atoms taken from ([1]); the amplitudes of coherent nuclear scattering were taken from ([10]). The nuclear-density projections were calculated on the "Kristall" computer. In the initial projection the main positive maxima were maxima corresponding to nitrogen and carbon atoms. Near the maxima of the heaviest nitrogen atoms, cutoff waves were arranged concentrically; their negative region occurred at a distance of 1 Å from the nitrogen atom (corresponding to the N—H distance). In this connection it did not appear possible to localize the hydrogen atoms reliably on this projection.

In order to estimate the influence of the cutoff waves, a theoretical series was constructed (from structural amplitudes calculated from the known positions of the C and N atoms; moreover the summation was limited only to those terms that were observed in the experiment). Analysis of the projection obtained in this way and comparison with the experimental projection made it possible to ascribe all the minima near atoms N_1 and N_2 to cutoff waves. Some of the minima near atoms N_3 and N_4 remained; these were associated with hydrogen atoms.

Fig. 2. Projection of the difference synthesis along the axis *oy*

In the subsequent calculations the coordinates of the C and N atoms from ([2]), obtained by X-ray diffraction from a three-dimensional synthesis, were used. The coordinates of the hydrogen atoms derived from the initial projection $\rho(x, z)$ by the method described above were also included. In doing this, an isotropic temperature correction with $B = 2$ was taken into account for all atoms. On the basis of these data, projections of the difference synthesis were constructed (from the structural amplitudes of the hydrogen atoms $F_H = F_{\text{exp}} - F_{\text{N,C}}$). Projections were constructed for two variants—I and II. In the case of imino variant II, when determining the sign of F_{exp}, hydrogen atoms H_4, H_3, and H_1 were placed in turn at atom N_2. Variant III was not included in the calculation, since the nuclear-density projection gave no grounds for placing hydrogen atoms near atom N_1; this was confirmed by the final calculations. From the projections of the difference series it was established that the only correct form of the dicyandiamide molecule is the amino form.

Table 1

Coordinates of atoms in the structure of dicyandiamide (space group C 2/c, position 8 *f*)

Atom	x	y	z	B
C_1	0,1335	0,1113	−0,0672	1,46
C_2	0,1151	0,1717	0,0907	2,24
N_1	0,1647	−0,0133	−0,1268	1,46
N_2	0,0902	0,2488	−0,0162	2,18
N_3	0,1811	−0,0400	0,1469	2,01
N_4	0,0710	0,3088	0,1440	2,01
H_1	0,1827	−0,0406	0,2283	2,60
H_2	0,2116	−0,2016	0,1135	4,00
H_3	0,0742	0,1496	0,2163	3,44
H_4	0,9184	0,4686	0,1098	4,20

—taken from ([2]); —determined by geometric analysis (see text).

In Fig. 1 is shown the projection of the nuclear density onto the plane (010), $\rho(xz)$; in Fig. 2, the projection of the difference synthesis. The coordinates of all atoms obtained from the projection are given in Table 1.

Further refinement of the structure, as well as determination of the individual isotropic temperature corrections, was carried out by the least-squares method on the M-20 computer at the Computing Center of Moscow State University. Two variants were specified—the amino and imino molecules. In both cases the reliability factor reached 16%. However, in imino variant II the method rea

responded to the introduction of an atom in an incorrect position by increasing, from cycle to cycle, its (and only its) individual temperature correction (which reached several tens). In the correct amino variant all temperature corrections

Fig. 3. Intermolecular bonds in dicyandiamide. A chain of molecules connected by hydrogen-bond bridges is shown. The molecules belong to different unit cells. Part of the molecules of the selected unit cell is not shown.

Figure 2: Fig. 3. Intermolecular bonds in dicyandiamide. A chain of molecules connected by hydrogen-bond bridges is shown. The molecules belong to different unit cells. Part of the molecules of the selected unit cell is not shown.

had quite rational values (see Table 1). This also favored the choice of the amino form of the molecule.

For solving the specific problem—the localization of hydrogen atoms for the purpose of correctly choosing the structural formula—the results of constructing a single projection are quite sufficient. The y coordinates of the hydrogen atoms,

Fig. 3. Intermolecular bonds in dicyandiamide. A chain of molecules connected by hydrogen-bond bridges is shown. The molecules belong to different unit cells. Part of the molecules of the selected unit cell is not shown.

given in Table 1, were determined by geometric analysis from the adopted N—H distance, assumed to be 1.03 Å (on the basis of literature data [11]), and also from the experimentally found N_3—H_1 distance obtained on the projection $\rho(xz)$, Fig. 1). The atoms H_1, H_2, and H_4 lie in the plane of the molecule, whereas the atom H_3 is displaced slightly out of this plane. A final resolution of the question of the coplanarity of the molecule requires the study of other projections.

In Figs. 1 and 2 it is seen that the minima corresponding to the hydrogen atoms H_2, H_3, and H_4 are elongated approximately perpendicular to the N—H bond. This permits the qualitative conclusion that there is substantial anisotropy of the thermal vibrations of the indicated hydrogen atoms: the amplitudes of vibration perpendicular to the N—H bond are greater than along it. The minimum corresponding to atom H_1 is more symmetric in shape. In agreement with this, the individual temperature correction for this atom, obtained by the least-squares method, also differs from the corrections for the other hydrogen atoms.

Localization of the hydrogen atoms makes it possible to construct the system of hydrogen bonds in the structure of dicyandiamide (Fig. 3). Neighboring molecules are connected by pairs of hydrogen bonds N_3—$H_2 \ldots N_1$ and N_4—$H_4 \ldots N_2$, so that infinite layers are formed in planes close to (310) and $(\bar{3}10)$. Along the direction of the oz axis, neighboring layers are connected by the hydrogen bonds N_4—$H_3 \ldots N_1$ and N_3—$H_1 \ldots N_1$, which in character are close to those found in the structure of urea [12].

We express our gratitude to A. I. Finkelshtein for providing an interesting object of study, and to Prof. G. S. Zhdanov and Z. V. Zvonkova for their constant interest in the work and valuable advice. We are also grateful to V. I. Andrianov, A. Tovbis, and A. Shorin for carrying out the computations.

Physicochemical Institute
named after L. Ya. Karpov

Received
6 XII 1963

REFERENCES

[1] E. W. Hughes, J. Am. Chem. Soc., **62**, No. 5, 1258 (1940).
[2] Z. V. Zvonkova, V. Ya. Krivnov, A. N. Khvatkina, DAN, **155**, No. 2 (1964).
[3] B. I. Sukhorukov, A. I. Finkelshtein, Optics and Spectroscopy, **6**, 5, 637 (1959); W. J. Jones, W. J. Orville-Thomas, Trans. Farad. Soc., **55**, 193 (1959).
[4] F. Pohl, J. Prakt. Chem., (2), **77**, 533 (1908).
[5] E. Bamberger, Ber., **16**, 1074 (1883).
[6] F. Chastellain, Helv. chim. Acta, **18**, 1287 (1935).
[7] M. T. Dangyan, Dokl. AN ArmSSR, **1**, 22 (1944).
[8] A. G. Owen, Tetrahedron, **14**, 237 (1961).
[9] G. P. Ozerov, S. V. Kiselev, and others, Probl. fiz. khim., issue 3, 201 (1963).
[10] D. E. Bacon, UFN, **81**, No. 2, 335 (1963).
[11] Tables of Interatomic Distances and Configuration in Molecules and Ions, London, 1958.
[12] J. E. Worsham, H. A. Levy, S. W. Peterson, Acta Crystallogr., **10**, 319 (1957).

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