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Note

X-Ray Diffraction Study of $\text{CH}_3\text{CN} \cdot 2\text{HBr}$

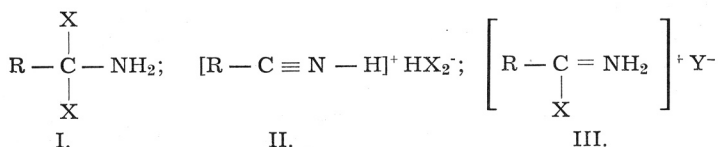
B. Matković*, S. W. Peterson, and J. M. Williams**

Washington State University, Pullman, Washington 99163, U. S. A.

Received February 10, 1967

Acetonitrile-2-(hydrogen bromide, hydrogen chloride and hydrogen iodide) were prepared first by A. Gautier¹ by saturating acetonitrile with hydrogen halide. He concluded that the compounds contained only one molecule of hydrogen halide. The chemical composition of the hydrogen bromide addition compound was subsequently determined by C. Engler², who established by analysis the correct chemical formula as $\text{CH}_3\text{CN} \cdot 2\text{HBr}$.

Conflicting views regarding the structures of the hydrogen halide addition compounds of acetonitrile have appeared in the literature. They can be represented by three different formulas:



where $\text{R} = \text{CH}_3$; $\text{X} = \text{Cl}, \text{Br}$ and I ; $\text{Y} = \text{Br}, \text{I}$ and SbCl_6 .

A. Hantzsch³ reasoned that the addition products of halogen acids with acetonitrile could be defined by formula II. L. E. Hinkel and G. L. Treharne⁴ reported that the structure of the dihydrogen chloride compound corresponds to formula I. F. Klages and W. Grill⁵ suggested types I and III as possible structures for acetonitrile-2-(hydrogen halides), but proposed that the probable structure is of type III. G. J. Janz and S. S. Danyluk⁶ found from infrared studies that the spectrum of solid $\text{CH}_3\text{CN} \cdot 2\text{HBr}$ was consistent with the structure of formula III. Their attempts to obtain the infrared spectrum of the solid hydrochloride compound were unsuccessful due to its unstability and low melting point. However infrared spectra of this compound, dissolved in anhydrous CH_3CN , obtained at molar concentrations of 0.5 and 1.5, led them to conclude that the structure of the $\text{CH}_3\text{CN} \cdot 2\text{HCl}$ complex corresponded to formula II. E. Allenstein and A. Schmidt⁷ concluded on the basis of infrared spectroscopic studies of $\text{CH}_3\text{CN} \cdot 2\text{HBr}$, $\text{CH}_3\text{CN} \cdot 2\text{HI}$ and $\text{CH}_3\text{CN} \cdot 2\text{HCl} \cdot \text{SbCl}_5$, that the structure of the hydrogen halide addition compounds of acetonitrile corresponds to formula III. In the hope that a direct crystal structure investigation could solve this rather complex problem, we have undertaken an X-ray diffraction study of $\text{CH}_3\text{CN} \cdot 2\text{HBr}$. Three-dimensional neutron dif-

Permanent address:

* Institute »Ruđer Bošković«, Zagreb, Yugoslavia.

** Argonne National Laboratory, Argonne, Illinois 60440, U. S. A.

fraction studies of $\text{CH}_3\text{CN}\cdot 2\text{HCl}$ were carried out simultaneously by J. M. Williams and S. W. Peterson⁸.

Crystals of $\text{CH}_3\text{CN}\cdot 2\text{HBr}$ were prepared by saturating acetonitrile with HBr at room temperature under anhydrous conditions. Spectroquality acetonitrile, *Matheson Coleman and Bell, Cincinnati, Ohio*, of less than 0.05% water content and hydrogen bromide gas, *The Matheson Company, Inc., East Rutherford, N. J.*, of 99.3% minimum purity were used. During the preparation HBr was absorbed rapidly and after a very short period colorless, transparent crystals appeared. These were flat prisms and were quite hygroscopic. Further examination was carried out under petrolatum and in sealed capillary tubes. Twinning was frequently observed and in several cases the presence of twin-crystals was obvious only from X-ray photographs.

TABLE I
Crystallographic Data

$\text{CH}_3\text{CN}\cdot 2\text{HBr}$	$\text{CH}_3\text{CN}\cdot 2\text{HCl}$
$a = 9.16 \pm 0.01$;	$8.72 \pm 0.01 \text{ \AA}$
$b = 7.24 \pm 0.01$;	$6.93 \pm 0.01 \text{ \AA}$
$c = 8.97 \pm 0.02$;	$8.63 \pm 0.01 \text{ \AA}$
$D_m = 2.21$;	1.43 g. cm.^{-3}
$D_x = 2.27$;	1.45 g. cm.^{-3}
Space group = $Pnma (D_{2h}^{16})$;	$Pnma (D_{2h}^{16})$
$Z = 4$;	4

The unit cell dimensions and space group were obtained from Weissenberg photographs and diffractometer measurements. The density was determined by flotation in $\text{CHBr}_3 + \text{CH}_3\text{CH}_2\text{I}$. The systematic absences of reflections indicated two possible space groups: $Pnma - D_{2h}^{16}$ or $Pn2_1a - C_{2v}^9$. The centro-symmetric group was chosen on the basis of structure analysis of $\text{CH}_3\text{CN}\cdot 2\text{HCl}$ ⁸. The crystallographic data of $\text{CH}_3\text{CN}\cdot 2\text{HBr}$ are listed in Table I along with data for $\text{CH}_3\text{CN}\cdot 2\text{HCl}$ for comparison. The coincidence of the possible space groups coupled with the similarity of the lattice constants suggested that the two compounds might be isomorphous.

The intensities of $h0l$ and $0kl$ reflections out to $2\theta = 45.5^\circ$ (reflections with higher 2θ values were undetectable) were collected from the sample mounted on a single crystal orienter using Mo $K\alpha$ radiation. The intensities were corrected for Lorentz and polarization factors in the usual way. Absorption corrections were calculated for each reflection using D. J. Wehe, W. R. Busing and H. A. Levy ORABS program⁹, and the structure factors derived. The parameters of Br, C and N atoms were obtained from Patterson and Fourier projections and refined by several least-squares cycles using the ORFLS program¹⁰ to the values listed in Table II. An isotropic temperature factor was varied for each atom. Atomic form factors were taken from the International Tables¹¹. Observed and calculated structure factors are listed in Table III. The residual $R (R = \sum_{hkl} ||F_o| - |F_c|| / \sum_{hkl} |F_o|)$ was 0.183 including unobserved reflections and 0.147 omitting unobserved reflections.

Precise refinement of the light-atom positional parameters was not possible based on the limited two-dimensional intensity data. The best agreement was with coordinates listed in Table II. Standard errors are given in parentheses and are somewhat large, as expected, for carbon and nitrogen atoms. The coordinates of these atoms though insufficiently accurate for calculation of correct bond lengths do determine that the molecular structure can be described by formula III. The atomic coordinates of $\text{CH}_3\text{CN}\cdot 2\text{HCl}$ are also listed in Table II for comparison. It was immediately obvious that the two compounds are structurally isomorphous and that further refinement should be carried out only on $\text{CH}_3\text{CN}\cdot 2\text{HCl}$.

The structure of $\text{CH}_3\text{CN}\cdot 2\text{HBr}$ is represented in projection in Fig. 1. All the atoms (except eight methyl hydrogen atoms) occupy special positions and

TABLE II
Atomic Coordinates

CH ₃ CN·2 HBr					CH ₃ CN·2 HCl				
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	B (Å ²)		<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	
Br 1	0.083 (.001)	0.250	−0.007 (.003)	5.4 (.3)	Cl 1	0.0951 (.0005)	0.250	−0.0084 (.0006)	
Br 2	0.214 (.004)	0.250	0.552 (.001)	4.5 (.9)	Cl 2	0.2171 (.0004)	0.250	0.5624 (.0005)	
C 1	0.290 (.025)	0.250	0.007 (.054)	6.1 (1.4)	C 1	0.2887 (.0006)	0.250	0.0070 (.0007)	
C 2	0.324 (.028)	0.250	0.175 (.009)	5.9 (2.0)	C 2	0.3528 (.0009)	0.250	0.1647 (.0008)	
N	0.366 (.001)	0.250	−0.120 (.011)	6.0 (.3)	N	0.3678 (.0004)	0.250	−0.1159 (.0005)	

CH₃CN·2 HBr: $R_1 = \sum_{hkl} ||F_o| - |F_c|| / \sum_{hkl} |F_o| = 0.183$ (including unobserved reflections) $R_2 = \sum_{hkl} ||F_o| - |F_c|| / \sum_{hkl} |F_o| = 0.147$ (omitting unobserved reflections)

TABLE III

Observed and calculated structure factors for CH₃CN·2 HBr (Structure factors for unobserved reflections were assigned the value 2.7 and designated by an asterisk.)

<i>h 0 l</i>	<i>F_o</i>	<i>F_c</i>	<i>h 0 l</i>	<i>F_o</i>	<i>F_c</i>	<i>h 0 l</i>	<i>F_o</i>	<i>F_c</i>	<i>0 k l</i>	<i>F_o</i>	<i>F_c</i>
2 0 0	80.6	−79.2	9 0 2	2.7*	7.0	4 0 5	23.0	−28.5	0 2 0	260.1	−275.5
4 0 0	2.7*	2.6	1 0 3	73.8	32.2	5 0 5	31.6	−31.4	0 4 0	146.9	158.5
6 0 0	75.9	−57.7	2 0 3	31.7	33.3	6 0 5	43.8	31.7	0 6 0	61.1	−79.1
8 0 0	29.1	−22.2	3 0 3	12.6	17.2	0 0 6	20.4	29.0	0 8 0	2.7*	33.6
10 0 0	31.3	18.1	4 0 3	38.5	−37.5	1 0 6	42.3	−45.8	0 1 1	53.2	46.5
1 0 1	56.8	62.9	5 0 3	90.8	−75.4	2 0 6	37.8	38.6	0 3 1	7.2	−33.1
2 0 1	29.6	20.3	6 0 3	53.5	43.4	3 0 6	38.8	41.0	0 5 1	13.4	19.2
3 0 1	89.9	84.8	7 0 3	2.7*	−4.0	4 0 6	29.7	−27.8	0 7 1	2.7*	−9.4
4 0 1	23.4	−26.0	8 0 3	41.2	−27.8	5 0 6	2.7*	−6.1	0 2 2	190.8	−179.9
5 0 1	147.2	−120.2	9 0 3	14.8	−11.6	6 0 6	20.5	−18.1	0 4 2	104.2	111.3
6 0 1	22.9	23.9	0 0 4	79.5	90.3	1 0 7	29.4	34.8	0 6 2	49.7	−57.8
7 0 1	2.7*	7.9	1 0 4	63.1	−65.0	2 0 7	24.4	26.3	0 1 3	140.8	111.2
8 0 1	19.3	−11.8	2 0 4	18.5	19.2	3 0 7	11.8	−13.6	0 3 3	82.7	−79.8
9 0 1	32.2	−21.7	3 0 4	23.8	66.0	4 0 7	2.7*	−12.0	0 5 3	37.2	46.5
0 0 2	203.1	220.5	4 0 4	8.1	−10.2	5 0 7	2.7*	−1.1	0 7 3	2.7*	−22.8
1 0 2	66.0	−65.6	5 0 4	22.4	−21.0	6 0 7	16.3	13.8	0 2 4	78.0	−77.3
2 0 2	32.1	−29.5	6 0 4	48.5	−39.5	0 0 8	2.7*	−1.9	0 4 4	42.4	51.0
3 0 2	66.8	65.5	7 0 4	2.7*	−0.6	1 0 8	8.5	−8.5	0 6 4	13.8	−26.9
4 0 2	7.7	6.0	8 0 4	18.0	−13.0	2 0 8	31.8	35.8	0 1 5	107.1	78.6
5 0 2	18.7	−18.9	9 0 4	2.7*	5.0	3 0 8	2.7*	16.0	0 3 5	71.6	−60.7
6 0 2	74.9	−58.4	1 0 5	57.0	56.7	4 0 8	2.7*	−23.7	0 5 5	34.7	37.6
7 0 2	2.7*	−5.5	2 0 5	33.6	40.5	5 0 8	2.7*	0.5	0 2 6	19.3	−24.6
8 0 2	24.2	−18.1	3 0 5	2.7*	−3.1				0 4 6	14.5	15.2
									0 1 7	37.5	31.1
									0 3 7	23.0	−24.9
									0 5 7	2.7*	15.9

lie in the mirror planes at $y = 1/4$ and $3/4$ of the space group $Pnma$. Atoms lying in the mirror plane at $y = 1/4$ are designated by shaded circles and those at $y = 3/4$ by open circles. The atoms which belong to CH₃·CBr·NH₂ groupings in the mirror plane at $y = 1/4$ are connected in the picture with straight lines, and those at $y = 3/4$ with dotted lines. The distance of 3.25 Å between N atom from CH₃·CBr·NH₂ groups and Br ions lying in the same mirror plane indicates probable hydrogen bonding. This was confirmed from the structure of CH₃CN·2 HCl where positions of all hydrogen atoms were

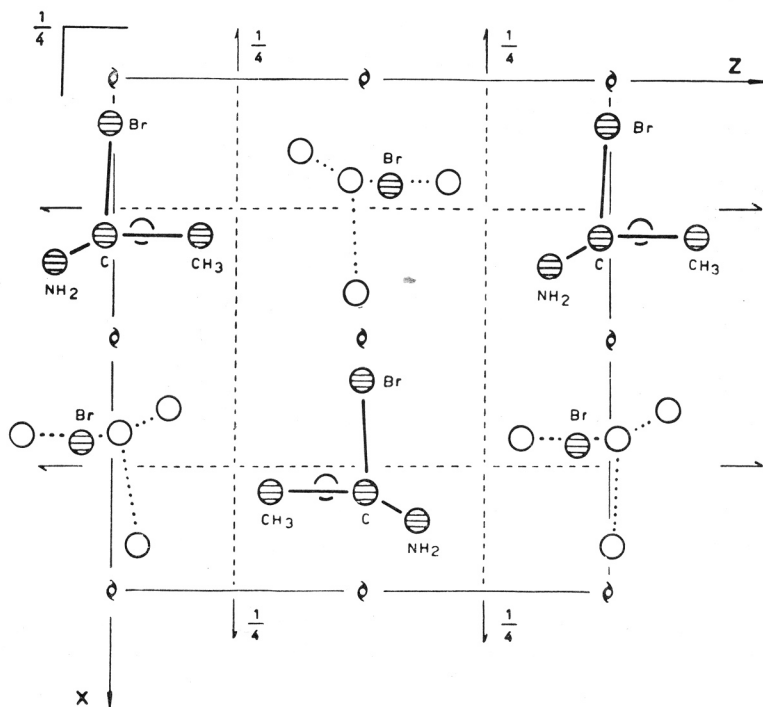


Fig. 1. Projection of the structure of $\text{CH}_3\text{CN}\cdot 2\text{HBr}$ on a plane normal to $[010]$. Atoms lying in the mirror plane at $y = 1/4$ are designated by shaded circles and those at $y = 3/4$ by open circles.

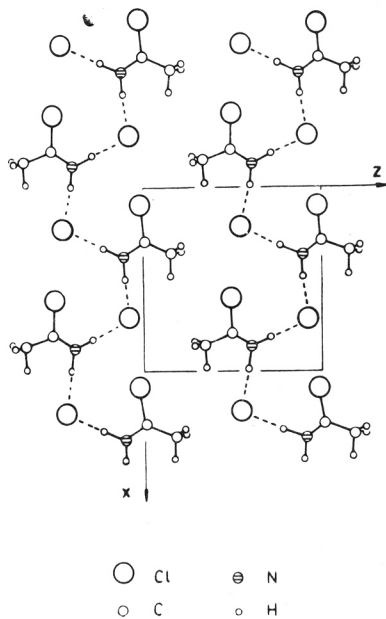


Fig. 2. $\text{N-H}\cdots\text{Cl}$ hydrogen bonding in the structure of $\text{CH}_3\text{CN}\cdot 2\text{HCl}$. Only these molecules are shown which lie in the mirror plane at $y = 1/4$.

determined. Fig. 2 shows the molecules of $\text{CH}_3\text{CN}\cdot 2\text{HCl}$ which lie in the mirror plane at $y = 1/4$. The atoms which belong to $\text{CH}_3\cdot\text{CCl}\cdot\text{NH}_2$ groupings are connected with straight lines and the $\text{N}-\text{H}\dots\text{Cl}$ hydrogen bonding by broken lines. The hydrogen bonds bind molecules lying in the mirror plane together forming planar chains. There is no contact between chains which are in the mirror plane at $y = 1/4$ and those at $y = 3/4$. The bond distances in $\text{CH}_3\text{CN}\cdot 2\text{HBr}$ are shown in Fig. 3. No significance should be attached to these interatomic distances, especially between carbon and nitro-

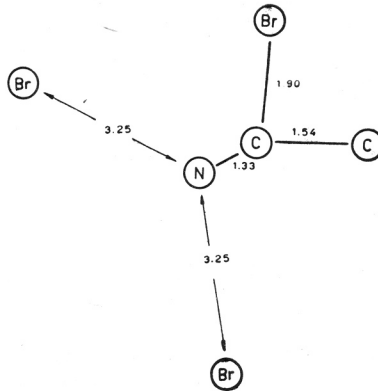


Fig. 3. The $\text{CH}_3\text{CN}\cdot 2\text{HBr}$ molecule showing bond lengths in angstroms.

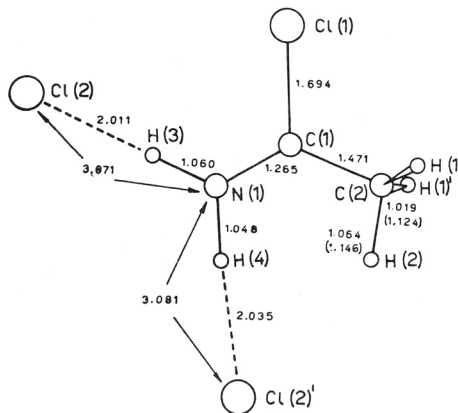


Fig. 4. The $\text{CH}_3\text{CN}\cdot 2\text{HCl}$ molecule showing bond lengths in angstroms. Bond distances in parenthesis are corrected for thermal motion.

gen atoms because of high standard deviation of their atomic coordinates. The structure analysis of $\text{CH}_3\text{CN}\cdot 2\text{HCl}$ permits a common treatment of the ste-

reochemistry of both isomorphous compounds and the Fig. 4 shows the bond distances in the $\text{CH}_3\text{CN}\cdot 2\text{HCl}$ molecule. The detailed description of this structure will be published elsewhere.

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IZVOD

Istraživanje $\text{CH}_3\text{CN}\cdot 2\text{HBr}$ metodom rendgenske difrakcije

B. Matković, S. W. Peterson i J. M. Williams

Struktura $\text{CH}_3\text{CN}\cdot 2\text{HBr}$ određena je iz dvodimenzionalnih podataka. Kristali su rompski, prostorna grupa $Pnma$, sa dimenzijama elementarne ćelije:

$$a = 9.16, \quad b = 7.24, \quad c = 8.97 \text{ \AA}, \quad Z = 4.$$

Na temelju kristalografskih podataka i koordinata atoma, ustanovljeno je da je spoj izomorfan sa $\text{CH}_3\text{CN}\cdot 2\text{HCl}$. Struktura odgovara formuli $(\text{CH}_3\cdot\text{CBr}\cdot\text{NH}_2)\text{Br}\cdot\text{N}-\text{H}\dots\text{Br}$ vodikove veze povezuju međusobno molekule koje leže u istoj zrcalnoj ravnini i stvaraju planarne lance. Nema nikakvih dodira među lancima u zrcalnim ravninama na $y = 1/4$ i $y = 3/4$.

WASHINGTON STATE UNIVERSITY
PULLMAN, WASHINGTON 99163, USA

Primljeno 10. veljače 1967.