MASTER

IS-T-439

THE CRYSTAL STRUCTURE
OF
QUINOLINIUM NONABROMOANTIMONATE(V), $(C_9H_7NH)_2Sb^VBr_9$
AND
THE REREFINEMENT OF THE MOLECULAR STRUCTURE OF
BETA-PICOLINE-N-OXIDE FUMARIC ACID ADDUCT

M. S. Thesis Submitted to Iowa State University, November 1970

Elwin Ray McAfee

Ames Laboratory, USAEC
Iowa State University
Ames, Iowa 50010

Date Transmitted: February 1971

PREPARED FOR THE U. S. ATOMIC ENERGY
COMMISSION DIVISION OF RESEARCH UNDER CONTRACT NO. W-7405-eng-82

IS-T-439

Available from
National Technical Information Service
Department A
Springfield, V. A. 22151
Price: Microfiche $0.95

THE CRYSTAL STRUCTURE
OF
QUINOLINIUM NONABROMOANTIMONATE(V), $(C_9H_7NH)_2Sb^VBr_9$
AND
THE REREFINEMENT OF THE MOLECULAR STRUCTURE OF
BETA-PICOLINE-N-OXIDE FUMARIC ACID ADDUCT

by

Elwin Ray McAfee

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

Major Subject: Physical Chemistry

Approved:

In Charge of Major Work

Head of Major Department

KJ Frey / gg Karas
Dean of Graduate College

Iowa State University
Of Science and Technology
Ames, Iowa

November 1970

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

THE CRYSTAL STRUCTURE
OF
QUINOLINIUM NONABROMOANTIMONATE(V), $(C_9H_7NH)_2Sb^VBr_9$
AND
THE REREFINEMENT OF THE MOLECULAR STRUCTURE OF BETA-PICOLINE-N-OXIDE FUMARIC ACID ADDUCT

Elwin Ray McAfee

ABSTRACT

The crystal structure of quinolinium nonabromoantimonate(V), $(C_9H_7NH)_2Sb^VBr_9$, has been determined by three dimensional x-ray analysis. The crystals were monoclinic, space group $P2_1/n$, $\underline{a} = 7.518 \pm 0.002$ Å, $\underline{b} = 11.316 \pm 0.005$ Å, $\underline{c} = 16.351 \pm 0.001$ Å, $\beta = 97.41 - 0.01^\circ$, and Z = 2. The structure was solved using initially an electron density map to locate the heavy atoms, and subsequent difference electron density maps to locate the light atoms. A full matrix weighted least squares refinement of 1867 observed reflections gave a final discrepancy index of $\underline{R} = 0.115$ for anisotropic refinement of the heavy atoms and isotropic refinement of the light atoms.

The structure consists of a slightly distorted octahedral $Sb^VBr_6^-$ ion--where the Sb sits on a center of symmetry--a linear Br_3^- ion, and two $(C_9H_7NH)^+$ cations. The Sb-Br dis-

tances corrected for independent thermal motion are 2.573 ± 0.003 Å, and 2.582 ± 0.003 Å. The Sb-Br...Br distances (3.743 ± 0.005 Å) do not appear short enough to account for any type of interspecies charge transfer interaction. It appears that the cation size is a strong influence on the packing position of the Br_3^- ion in the crystal lattice.

The crystal structure of beta-picoline-N-oxide fumaric acid adduct, $2(C_6H_7NO):(C_4H_4O_4)$, was originally solved by Byron T. Gorres using three dimensional x-ray analysis techniques. The crystals were monoclinic, space group $P_{2_1/c}$, $\underline{a} = 3.888 \pm 0.003$ Å, $\underline{b} = 14.194 \pm 0.010$ Å, $\underline{c} = 14.663 \pm 0.011$ Å, $\beta = 98.85 - 0.1^\circ$, and Z = 2. The structure was solved using a symmetry map-frequency check procedure in conjunction with a roving molecular fragment. However, further refinement was made using a full matrix least squares program modified to include a secondary extinction parameter. The final conventional discrepancy index was $\underline{R} = 0.052$ and the weighted discrepancy index $\underline{Rw} = 0.037$ for the 533 observed reflections measured by scintillation counter methods.

The beta-picoline-N-oxide and the fumaric acid moieties are held together by hydrogen bonding forces and are planar to within 0.020 and 0.001 Å, respectively. A strong hydrogen bond between the OH group of the acid and the oxygen of the beta-picoline-N-oxide ring appears to hold the adduct together. This short O...O distance of 2.517 ± 0.006 Å lies within a range characteristic for a symmetric hydrogen bond. However, this hydrogen could not be reliably located.

THE STRUCTURE OF QUINOLINIUM NONABROMOANTIMONATE(V)

Introduction

The crystal structure investigation of quinolinium nonabromoantimonate(V), QAB, was undertaken as part of a series of investigations of halo-coordinated antimony compounds being performed at this laboratory.[1-8] A series of intervalence antimony bromide complexes of varying stoichiometries have been investigated in an attempt to relate their crystal structures and charge transfer properties, and to evaluate the effects of cation size, type, and stereochemistry on the antimony bromide anion and on the resulting solid state structure.

Spectral studies and other physical property measurements indicated that QAB resembled the other intervalent antimony bromide complexes, particularly the subgroup which exhibited color changes as temperature was lowered.

Experimental

The quinolinium antimony bromide salt was prepared following the procedure developed by S. L. Lawton.[3] The salt was recrystallized as follows: a small amount of the compound was digested in approximately 4-5 ml of warm concentrated hydrobromic acid (48%) at a temperature slightly below the boiling point of the solution. Bromine vapor was continuously passed over the top of the beaker to prevent debromination. After digestion was complete, the solution was allowed to cool slowly while the bromine atmosphere was retained. Reddish-black plate-like crystals slowly formed.

Crystal Data

Quinolinium nonabromoantimonate(V), $(C_9H_7NH)_2SbBr_9$, F.W. = 1103.3 g/mole, monoclinic, space group P_{2_1}/n, lattice parameters[9] at 25°C--a = 7.518 ± 0.002 Å, b = 11.316 ± 0.005 Å, c = 16.351 ± 0.001 Å, β = 97.41 ± 0.01°, V = 1391 Å, d_{obsd} = 2.65 g/ml--by flotation method using mixtures of diodomethane (d = 3.30) and methylene chloride (d = 1.331), d_{calc} = 2.67 g/ml for Z = 2 formula units per unit cell, F(000) = 1012 e^-, μ = 142.08 cm^{-1}

The preliminary crystal symmetry was determined from precession photographs which showed 2/m Laue symmetry and systematic conditions limiting possible reflections: 0k0, k = 2n, and h0l, h + l = 2n. The lattice parameters and associated errors were determined by a left-right, top-bottom beam splitting technique of twelve high order reflections measured on a previously aligned Hilger-Watts four circle diffractometer.

Collection and Reduction of X-Ray Intensity Data

Complete three-dimensional x-ray diffraction intensity data were taken at room temperature (approximately 25°C) with zirconium-filtered molybdenum K-α radiation from a plate-like crystal of dimensions 0.32 X 0.192 X 0.096 mm. The crystal was sealed in a 0.2 mm Lindemann glass capillary and mounted such that the a* axis was coincident with the phi axis. A fully automated Hilger-Watts four-circle diffractometer equipped with scintillation counter and interfaced to a SDS-910 computer in a real time mode was used for data collection. The stationary crystal-stationary counter technique with take-off angle of 4.5° was employed to collect all data in the hkl and the $hk\bar{l}$ octants within a 2θ sphere of 50°.

The main reflection data were collected as peak-height data where a ten second count was employed on the peak maxima. Background measurements were made on both sides of the peak. The intensity value of each reflection was corrected for background, Lorentz-polarization, and converted to its integrated value. Three strong reflections were chosen as standards and remeasured periodically throughout the data collection process, and showed essentially no variation.

Approximately 100 reflections at various angular settings were also measured using step-scan techniques to construct an integrated intensity-peak height conversion curve. This curve was found to be dependent only on 2θ with step-scan/peak height ratio ranging from 0.80 at low theta, to 0.98 at large values of theta (26°).

Determination of the Structure

Since there are only two molecules per unit cell and four general positions in the space group $P2_1/n$, the antimony atoms must lie on centers of symmetry. An electron density map computed with antimony atoms at (0,0,0) and ($\frac{1}{2}$,$\frac{1}{2}$,$\frac{1}{2}$) revealed an octahedron of bromines around the antimony (see Figure 2a), and Br_3^- groups (see Figure 2b) centered about the centers of symmetry at ($\frac{1}{2}$,$\frac{1}{2}$,0) and (0,0,$\frac{1}{2}$). Isotropic refinement[10] produced a conventional discrepancy index, $R = \sum|(|F_o| - |F_o|)/\sum|F_o|$, of 21%.

A difference electron density map was then computed and eight of the ten light atoms in the quinolinium group (see Figure 2c) were readily located. These were input into the least squares refinement and positions of the other two carbon atoms were found on a subsequent difference map. Refinement of the heavy atoms (Sb,Br) anisotropically and the carbons isotropically lowered the agreement factor to 11.5%.

The x-ray scattering factors of Doyle and Turner[11] were used for the non-hydrogen atoms and corrections were applied to the real and imaginary parts of anomalous dispersion[12] for the antimony and bromine atoms.

Final values of the positional and thermal parameters are given in Tables 1 and 2, respectively, and the observed and calculated structure factors are given in Table 3.

Description of the Structure

The $Sb^VBr_6^-$ ion and the Br_3^- ion both occupy crystallographic centers of symmetry while the two cations occupy general positions related by a center of symmetry within the unit cell as illustrated in Figure 1. The bromine coordination around the antimony atom consists of a slightly distorted octahedral configuration. The bromine-antimony-bromine angles are very close to the ninety degrees expected for an octahedron. Two significantly different Sb-Br bond lengths are found to be 2.531 ± 0.002 and 2.550 ± 0.003 Å when no thermal correction is applied to the Sb-Br distances (see Table 4). However, when an independent thermal motion correction is applied to the Sb-Br distances four of the six Sb-Br distances approach 2.573 ± 0.003 Å while the other two Sb-Br distances are found to be 2.582 ± 0.003 Å. The somewhat longer Sb-Br distance can be attributed to ionic van der Waal contact with the cation. The Sb-Br distances are comparable to those distances found in the α-picolinium nonabromoantimonate(V) structure[5]--2.547 ± 0.003 and 2.565 ± 0.003 Å, respectively.

The uncorrected Br-Br distances in the Br_3^- ion are found to be 2.541 ± 0.003 Å which compares favorably with those distances found in the α-picolinium nonabromoantimonate(V)--APAB--and in the $(CH_3)_3NHBr_3$[13] structures--2.543 ± 0.002 Å and 2.53 to 2.54 Å, respectively. When thermal corrections were applied the Br-Br distances were found to be 2.587 ± 0.003 Å in QAB and 2.554 ± 0.002 Å in APAB

The closest van der Waal contact distance of a Br coordinated to the Sb and a Br of the Br_3^- group is 3.743 ± 0.005 Å, compared to 3.491 ± 0.002 Å in the α-picolinium nonabromoantimonate(V)--the sum of the Pauling van der Waal's radius of bromine is 3.90 Å. The Sb-Br...Br-Br-Br angle in APAB is nearly linear, 166.87 ± 0.06°, while the Sb-Br...Br-Br-Br angle in QAB was found to be 56.24 ± 0.08°. Thus, a nearly linear charge transfer path was a possibility in the APAB structure through the Br-Sb-Br...Br-Br-Br...chains in the (120) crystal planes with the cation forming a sandwich about the -Br...Br- bridge. However, in the QAB structure, the packing effects of the cation are such that the Br_3^- group no longer forms a nearly linear system with the $SbBr_6^-$ ion. This effect is further exemplified by noticing the relatively long van der Waal contact distance of 3.975 ± 0.029 Å between the cation and the terminal Br of the Br_3^- group compared to the closest van der Waal contact distance of 3.68 ± 0.02 Å in the APAB structure. The closest $SbBr_6^-$...cation van der Waal distance in QAB is 3.699 ± 0.035 Å which compares well to the closest van der Waal distance in APAB of 3.79 ± 0.02 Å. The cation distances and angles (Table 4) agree well with what one would expect to find for this essentially planar organic species.

Conclusion

It has been shown in the QAB structure that the Sb-Br...Br distances do not appear short enough to account for any type of interspecies charge transfer interaction. It has also been shown that the size of the cation does have an influence on the packing position of the Br_3^- ion in the crystal lattice, in comparison to the APAB structure.

This structure determination in conjunction with the tetraethylammonium hexabromoantimonate(V)[14] determination strongly suggests that the intense color of these and other antimony(V) complexes must be the result of intraspecies charge transfer and not interspecies effects.

Table 1. Final positional parameters and estimated standard errors of QAB[a]

Atom	X	Y	Z
Sb[b]	0	0	0
Br1	2740(3)	1351(2)	0318(1)
Br2	-2023(3)	1706(2)	0312(1)
Br3	0279(3)	-0578(2)	1522(1)
Br4[b]	5000	5000	0
Br5	5431(4)	3864(2)	1364(1)
C1	5467(31)	8822(22)	1625(15)
C2	4495(29)	8948(23)	3002(13)
C3	5831(37)	0651(23)	2339(17)
C4	3943(33)	7750(22)	2921(14)
C5	5000(40)	7732(26)	1560(19)
C6	5669(42)	1294(29)	3020(24)
C7	4262(40)	7120(28)	2218(20)
C8	4866(39)	0796(34)	3702(18)
C9	4321(41)	9593(31)	3749(20)
C10	5266(29)	9489(22)	2329(15)

[a] Numbers in parentheses represent standard deviations occurring in the last digit of the parameter.

[b] Atom positions are fixed by symmetry considerations.

Table 2. Final thermal parameters and estimated standard errors of QAB

Anisotropic thermal parameters[a]

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Sb	0128(4)	0067(1)	0021(1)	-0004(2)	0000(1)	-0003(1)
Br1	0171(5)	0107(2)	0034(1)	-0047(2)	0007(1)	-0011(1)
Br2	0187(5)	0088(2)	0036(1)	0027(3)	0003(1)	-0006(1)
Br3	0220(5)	0084(2)	0022(1)	-0006(2)	-0003(1)	0004(1)
Br4	0188(7)	0087(3)	0043(1)	-0011(3)	0003(2)	-0020(1)
Br5	0241(6)	0123(3)	0045(1)	-0015(3)	-0006(2)	-0005(1)

Isotropic thermal parameters[b]

Atom	B	Atom	B
C1	5.9 (0.5)	C6	6.8 (0.7)
C2	4.2 (0.5)	C7	7.0 (0.7)
C3	5.7 (0.6)	C8	6.9 (0.7)
C4	4.4 (0.5)	C9	6.9 (0.7)
C5	5.8 (0.6)	C10	3.8 (0.4)

[a] Anisotropic temperature form = $\exp(-\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$.
[b] All atoms in organic ring were refined as carbon atoms.

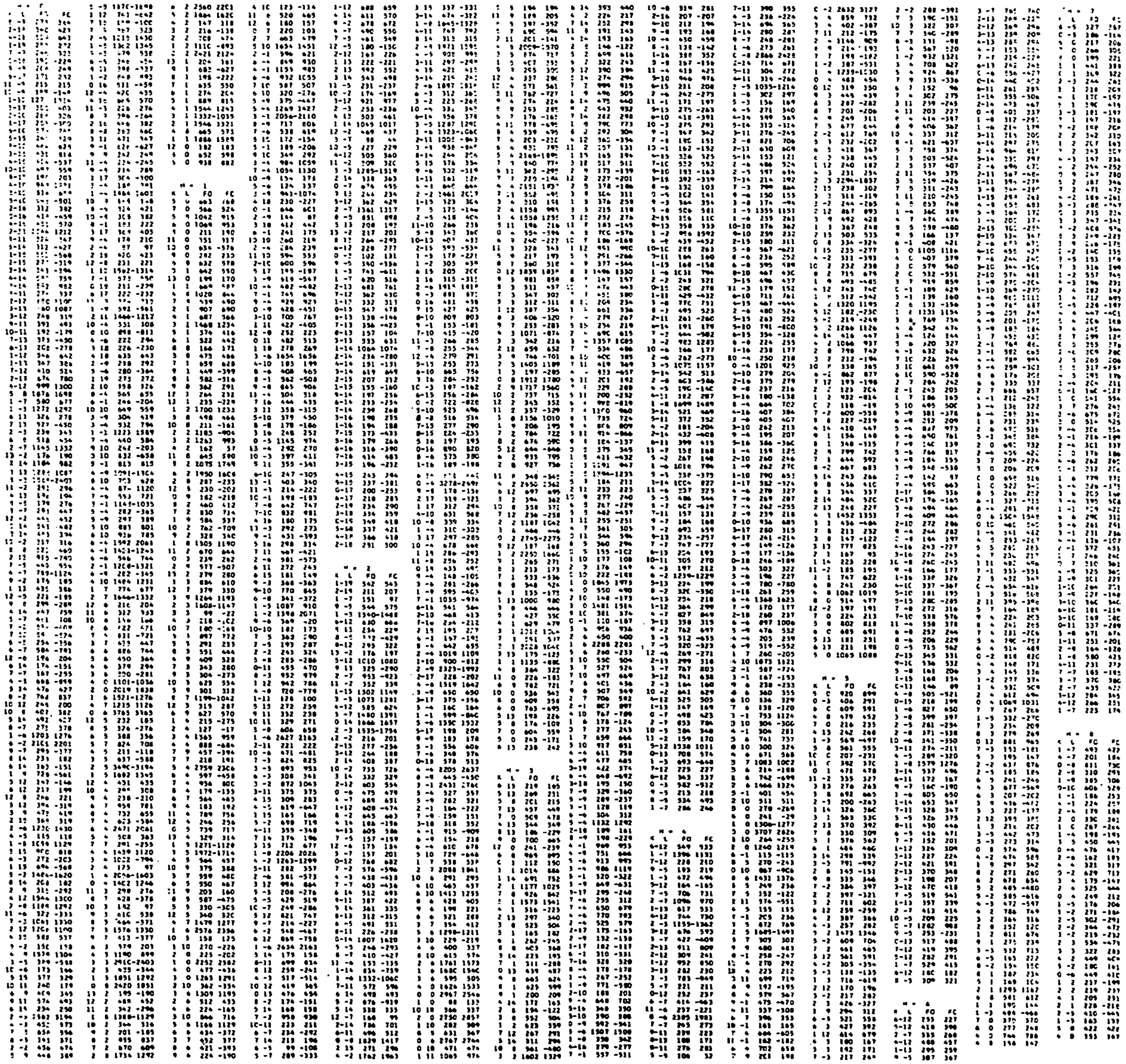

Table 3. Final values of observed and calculated structure factors of QAB

Table 4. Selected internal distances and angles of QAB

Atom	Distances (Å)[a,b]	
	uncorrected	corrected
Sb-Br1	2.543(3)	2.582(3)
Sb-Br2	2.537(3)	2.573(3)
Sb-Br3	2.535(2)	2.574(2)
Sb-Br4	6.770(5)	6.783(5)
Sb-Br5	6.162(6)	6.180(6)
Br1-Br2	3.555(6)	
Br1-Br3	3.584(4)	
Br1-Br4	4.513(4)	
Br1-Br5	3.753(4)	
Br2-Br3	3.547(4)	
Br2-Br4	3.585(4)	
Br4-Br5	2.541(3)	2.587(3)
C2-Br5[c]	3.93(2)	
C3-Br1[c]	3.62(3)	
C3-Br2[c]	3.61(3)	
C3-Br3[c]	3.90(3)	
C3-Br5[c]	3.79(3)	
C4-Br3[c]	3.67(3)	
C4-Br5	4.06(3)	
C8-Br1	3.82(3)	
C8-Br5	3.96(2)	
C9-Br3[c]	3.69(4)	
C9-Br5	3.97(3)	

[a] The bond distances have been corrected for independent thermal motion.

[b] Numbers in parentheses represent standard deviations occurring in the last digit of the parameter.

[c] Symmetry operation $\frac{1}{2} + X$, $\frac{1}{2} - Y$, $\frac{1}{2} + Z$ has been applied to this atom position.

Table 4 (continued)

Atom	Distances (Å)
C1-C2	1.45(3)
C2-C3	1.41(4)
C3-C4	1.40(4)
C4-C5	1.43(4)
C5-C6	1.27(4)
C6-C7	1.39(3)
C7-C8	1.38(4)
C8-C9	1.33(4)
C9-C10	1.42(5)
C2-C7	1.42(3)

Atom	Angle (°)
C1-C2-C3	120.3(2.4)
C2-C3-C4	118.4(2.3)
C3-C4-C5	118.4(2.7)
C4-C5-C6	122.4(3.0)
C5-C6-C7	122.1(2.7)
C6-C7-C8	56.6(1.4)
C6-C7-C2	118.8(2.4)
C7-C8-C9	56.6(2.1)
C8-C9-C10	121.7(3.2)
C8-C9-C1	69.6(2.1)
C10-C1-C2	58.1(1.5)
Br1-Sb-Br2	88.80(0.12)
Br1-Sb-Br3	89.78(0.10)
Br2-Sb-Br3	88.73(0.10)
Br1-Br4-Br5	56.24(0.08)
Br2-Br4-Br5	69.65(0.11)
Br3-Br4-Br5	47.48(0.08)
Sb-Br4-Br5	65.41(0.09)
Br5-Br4-Br5	180.00(0.00)

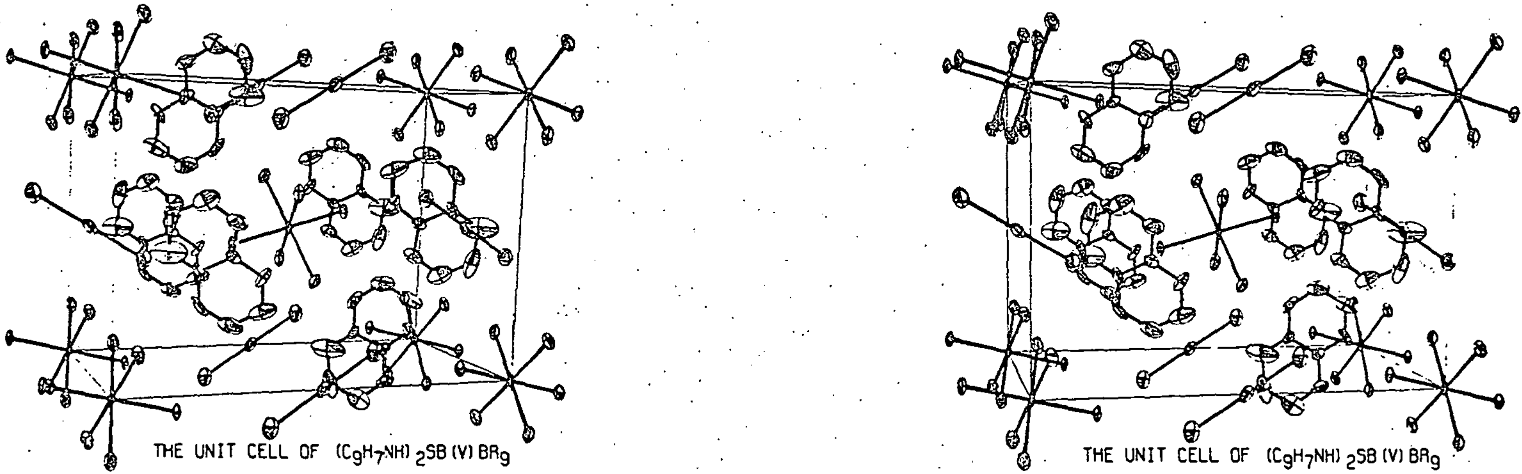

Figure 1. Unit cell drawing of quinolinium nonabromoantimonate(V)

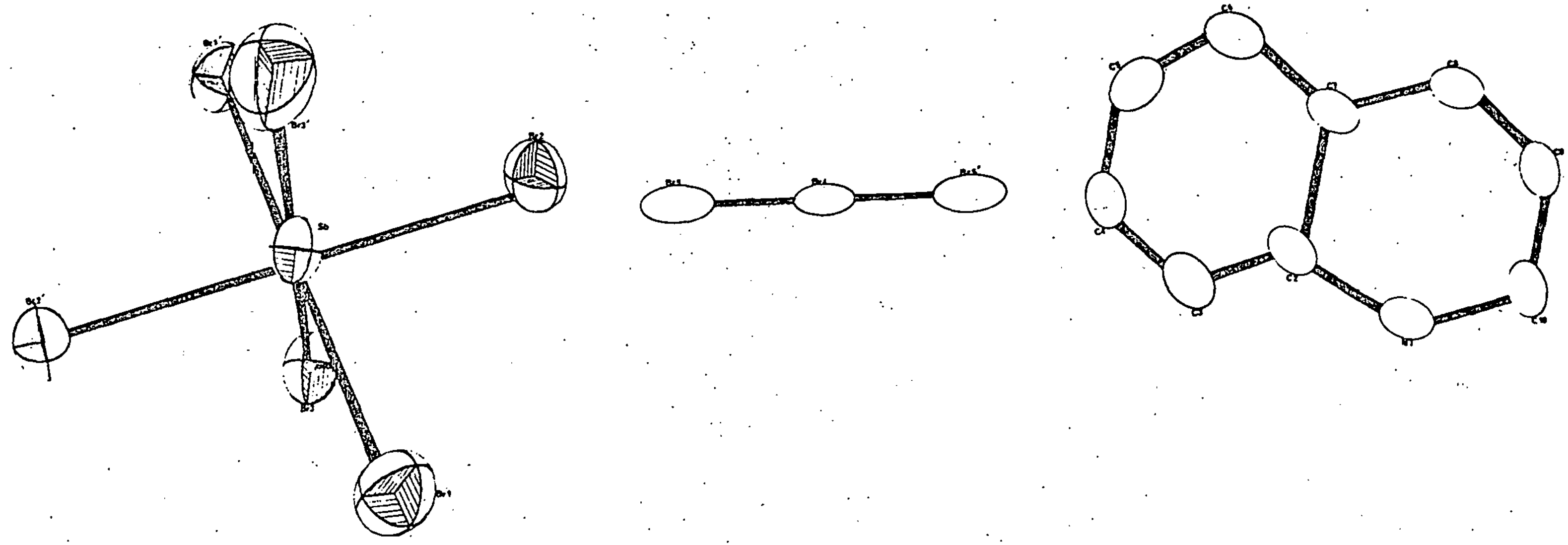

Figure 2. Ionic fragments of the structure: a) $SbBr_6^-$, b) Br_3^-, and c) $C_9H_7NH^+$

THE REREFINEMENT OF THE MOLECULAR STRUCTURE OF BETA-PICOLINE-N-OXIDE FUMARIC ACID ADDUCT

Introduction

E. C. Taylor and R. O. Kan have found that a two:one adduct of beta-picoline-N-oxide and fumaric acid can be prepared by refluxing stoichiometric ratios of the two in water. Their spectral studies (NMR, infrared, and ultraviolet) of the adduct indicated only a mixture of the two reactants. Since the adduct formed stable colorless crystals, the crystal structure investigation was undertaken by Byron T. Gorres[15] to obtain more complete structural information concerning this adduct. However, in resolving the structure, twelve large reflections displayed large differences between F_o and F_c which were characteristic of secondary extinction. The rerefinement of the beta-picoline-N-oxide fumaric acid adduct was then undertaken to establish that a secondary extinction correction would give better resolution of the structure, particularly in the region where the ninth hydrogen between the oxygen of the beta-picoline-N-oxide ring and the oxygen of the fumaric acid demonstrated likely possibilities of a strong hydrogen bond.

Experimental

Crystal data:

β-picoline-N-oxide fumaric acid adduct, $C_{16}H_{18}N_2O_6$, F.W. = 334.3 g/mole, monoclinic, $P2_1/c$, $\underline{a} = 3.888 \pm 0.003$ Å,

$\underline{b}$ = 14.194 ± 0.010 Å, $\underline{c}$ = 14.663 ± 0.011 Å, β = 98.85 ± 0.1°, V = 799.9 - 1.1 Å^3, d_{obsd} = 1.36 g/ml (by flotation), d_{calc} = 1.388 ± 0.001 g/ml for Z = 2 formula units per unit cell, μ = 1.14 cm^{-1}, Mo K-α(λ = 0.71069 Å), secondary extinction coefficient = 3824.43

Samples of the adduct were kindly supplied by R. O. Kan. Colorless needle crystals were obtained by recrystallization from an ethanol solution. Precession and Weissenberg photographs exhibited 2/m Laue symmetry with the following systematic absences: 0$\underline{k}$0 when $\underline{k}$ = 2n + 1, and $\underline{h}$0$\underline{l}$ when $\underline{l}$ = 2n + 1. These conditions uniquely specified the monoclinic space group $P2_1/c$. The unit cell dimensions and their standard deviations were obtained from a measurement of high order reflections on a General Electric XRD-5 equipped with single crystal orienter and scintillation counter.

Integrated intensities were also measured on this unit using the theta-two theta scan technique (2°/min) with backgrounds measured for 100 seconds at both ends of the scan. A crystal of approximate dimensions 0.24 X 0.24 X 0.36 mm was mounted such that the (010) axis was coincident with the phi axis. All reflections having sin θ/<0.538 (45° in 2θ) were measured using Zr-filtered Mo K-α radiation. As many equivalent reflections as possible (approximately 80%) were also measured and an average data set was obtained. Of the 1103 non-equivalent reflections 534 reflections exhibited observed intensities.

Data were corrected for Lorentz-polarization effects. In order to account for secondary extinction effects, an absorption correction was made; transmission factors ranged from 0.95 to 0.97.

Determination of the Structure

Since there are only two formula weights per unit cell, the adduct moiety must possess a center of symmetry. The size of the unitary structure factor ($U = 0.73$) of the 102 reflection indicated that most of the atoms lie in this plane.

A sharpened three-dimensional Patterson map was computed. Initial superposition attempts produced maps which were difficult to interpret and yielded no refineable model. Symbolic addition methods and vector verification methods were tried but again proved to be unsuccessful. A major difficulty appeared to result from the fact that all atoms in the structure resided on or close to the 102 plane, giving rise to very densely packed regions in the Patterson function.

Our vector verification results coupled with information obtained from the arrangement of Patterson peaks around the origin indicated a very probable orientation of the *beta*-picoline-N-oxide ring. This eight atom group was then moved over a symmetry map.[16-18] To simplify computations, a bivalued Patterson map and resultant symmetry map were used. Each point in Patterson space was assigned a value of one if it exceeded two-thirds of the carbon-carbon peak height; otherwise it was assigned a value of zero. A point representing the origin of the beta-picoline-N-oxide group was considered acceptable only if (i) a one occurred at all positions in the symmetry map corresponding to the atom positions in the group, and (ii) a one occurred at all positions in the Patterson representing vectors between the group and its symmetry related positions. A value was then assigned to each of the positions satisfying the above conditions by the use of the frequency check procedure.[19] This procedure readily and clearly indicated the correct position for this group in the unit cell. A subsequent electron density calculation indicated the positions of the fumaric acid moiety and this model gave an initial discrepancy factor ($R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$) of 0.34. Isotropic refinement immediately reduced this value to 0.13, using a weighting scheme described previously[20] based on the size of F_o.

A difference electron density map at this point indicated considerable anisotropic motion and also plausible positions for all but one of the hydrogen atoms (see below). These atoms were added and all non-hydrogen atoms were refined anisotropically and the positional parameters of the eight hydrogen atoms were refined with a constant isotropic thermal parameter, B, of 3 $Å^2$. The calculated structure amplitudes were corrected for real and imaginary parts of anomalous dispersion[12] due to the non-hydrogen atoms. The large structure factors showed evidence of secondary extinction and a secondary extinction parameter[21] (3824.43) was included in the refinement. The weights were checked by plotting $\overline{\omega\Delta}^2$ against $\sin\theta/\lambda$ and a small adjustment was subsequently made. One reflection, the (306) was excluded due to high background. The final values of R and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}}$, were 0.052 and 0.037, respectively.

The x-ray scattering factors of Doyle and Turner[11] were used for the non-hydrogen atoms. For hydrogen, the contracted form of Stewart, Davidson, and Simpson[22] was used. The final positional and thermal parameters and their standard deviations as determined from the inverse matrix of the final least squares cycle are given in Table 5 and Table 6, respectively. In Table 7 are given the final values of the observed and calculated structure factors (X10).

Description of the Structure

Figure 3 illustrates the whole beta-picoline-N-oxide fumaric acid adduct. The center of symmetry of the molecule is located between C_9 and C_9'. The adduct appears to be held together by a strong hydrogen bond between the OH group of the acid and the oxygen of the beta-picoline-N-oxide ring. The $O_8 \cdots O_{12}$ distance is 2.517 ± 0.006 A and the $N_1\text{-}O_8 \cdots O_{12}$ angle is 133.5 ± 0.4°. The $O_8 \cdots O_{12}$ distance lies within the range that Hamilton[23] would classify as a probable symmetric hydrogen bond. However, it was just this hydrogen which could not be reliably located. There appeared to be some diffuse peaks around the oxygens but no chemically satisfactory results were obtained on further attempts to refine any of these positions. Therefore, this hydrogen was deleted from further refinement, and no additional information was obtained relative to the presence or absence of a symmetrical hydrogen bond.

The only other close contact for hydrogen bonding is between the C-H of the epsilon carbon to the other carboxyl oxygen of the fumaric acid. The O...H distance is 2.5111 ± 0.070 Å (C-H...O angle is 162.4 ± 7.0°) and may be indicative of an additional weak hydrogen bond. Such a second hydrogen bond could account for all the non-hydrogen atoms of the adduct being within 0.02 Å of the least squares plane (Table 8). The beta-picoline-N-oxide and the fumaric acid moieties are planar to within 0.020 and 0.001 Å, respectively. All non-hydrogen atoms lie approximately in the 102 planes. These planes are separated by a distance of 3.2 Å. Of course, packing effects may also cause the observed planarity of the adduct. A projection of the electron density function along the a-axis is given in Figure 4.

The internal distances and angles (Figure 3 and Table 9) for the fumaric acid specie appears to be consistent with the distances reported in the literature.[24]

Conclusion

The adduct formed by fumaric acid and *beta*-picoline-N-oxide has been shown to be held together by hydrogen bonding forces accounting for the similarity in spectra between the atoms of the reactants and the product. The usefulness of a symmetry map-frequency check procedure in conjunction with a roving molecular fragment has been illustrated.

An accurate determination of the hydrogen atom position, say by neutron diffraction techniques, could provide useful information as to the presence or absence of a symmetrical hydrogen bond.

Table 5. Final positional parameters and estimated standard errors of beta-picoline-N-oxide fumaric acid adduct[a,b,c]

Atom	X	Y	Z
N1	2275(17)	4047(3)	3972(4)
C2	2540(21)	5014(4)	3912(6)
C3	3716(21)	5388(5)	3159(5)
C4	4605(24)	4841(5)	2444(6)
C5	4304(21)	3879(5)	2554(5)
C6	3192(24)	3503(5)	3298(6)
C7	4073(2)	6485(0)	3151(0)
O8	1109(15)	3698(3)	4688(3)
C9	-0286(22)	0411(4)	5171(5)
C10	0605(24)	1291(5)	4704(6)
O11	1696(16)	1326(3)	3990(3)
O12	0004(17)	2046(3)	5196(4)
H1	194(17)	544(4)	458(5)
H2	275(25)	656(6)	274(6)
H3	319(18)	668(4)	393(5)
H4	592(18)	639(5)	260(5)
H6	494(17)	350(4)	194(5)
H7	237(19)	296(4)	339(5)
H8	-158(18)	045(4)	581(4)

[a] All non-hydrogen atom positional parameters ($X10^4$).

[b] All hydrogen atom positional parameters ($X10^3$).

[c] Numbers in parentheses represent standard deviations occurring in the last digit of parameter.

Table 6. Final thermal parameters and estimated standard errors[a]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N1	934(74)	33(4)	50(4)	-16(13)	43(15)	-28(3)
C2	779(89)	20(4)	48(5)	6(14)	44(17)	1(3)
C3	663(69)	31(4)	48(4)	-26(16)	26(14)	14(4)
C4	915(95)	40(4)	55(5)	19(15)	62(19)	-4(4)
C5	1001(93)	38(4)	45(5)	11(1)	89(18)	-8(3)
C6	1227(101)	25(4)	52(5)	-11(17)	98(19)	4(4)
C7	1187(138)	28(4)	77(7)	21(19)	98(23)	9(5)
O8	1549(73)	28(2)	57(3)	-13(12)	159(13)	5(2)
C9	881(81)	30(4)	61(5)	-30(18)	87(17)	5(5)
C10	892(87)	29(4)	51(5)	-38(16)	32(18)	1(5)
O11	1575(75)	30(2)	57(3)	-26(12)	128(14)	0(3)
O12	1601(72)	32(3)	60(3)	-26(11)	158(13)	-7(2)

H1-8 have isotropic temperature factors fixed at 3.0000

---

[a] Anisotropic temperature form = $\exp(-\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$.

H	L	FO	FC
K = 0			
H	L	FO	FC
-1	10	95	93
-3	4	89	87
1	10	88	85
2	9	86	83
-1	4	84	67
0	12	84	83
-4	6	83	-67
1	12	76	-66
2	6	75	77
-2	8	69	66
0	6	65	67
-3	2	65	59
-2	2	59	43
1	8	57	36
3	0	56	59
2	2	51	35
1	2	2085	2056
2	4	643	653
0	4	374	366
-1	2	335	305
-1	12	338	-357
-2	13	297	-322
0	2	240	246
-1	5	253	251
0	14	252	-244
1	4	212	200
0	8	209	239
-1	8	196	195
1	0	181	152
-3	8	178	-176
-2	6	163	160
-2	4	160	148
1	6	158	146
0	10	146	137
K = 1			
H	L	FO	FC
-2	8	145	-136
-1	5	143	-153
-2	12	140	-159
-1	11	134	-125
-2	13	112	119
0	4	133	-145
2	3	163	-166
0	1	167	146
1	5	191	-206
3	3	206	-203
-3	13	114	-121
2	2	235	-243
0	4	263	267
0	2	350	352
-1	14	116	-119
-1	2	343	341
0	3	634	-659
-1	1	813	-835
1	3	451	-463
2	1	452	-470
0	12	33	22
0	13	27	15
0	11	50	52
1	3	49	48
2	3	45	46
-3	9	47	-47
0	14	44	36
-3	4	44	30
2	4	41	28
0	8	38	-53
3	2	59	-45
-3	1	65	-61
1	7	63	-57
-1	13	62	-55
-3	8	62	49
2	7	65	-59
-1	12	66	60
0	7	69	-77
0	9	69	-66
-3	5	58	-63
-1	7	74	-84
-2	11	72	-67
-2	10	75	66
1	4	76	80
3	4	73	-82
-1	15	82	84
1	8	81	-81
-3	12	81	-78
1	6	79	83
-2	3	124	-126
-3	11	123	116
1	1	122	120
1	13	83	71
0	13	85	-74
-3	7	87	-85
-1	6	92	-99
-2	7	91	-94
-2	14	97	-94
K = 2			
H	L	FO	FC
-1	2	91	-77
-3	8	85	-89
-2	2	126	-121
1	8	102	-97
-2	10	116	-120
-2	12	82	72
0	13	71	62
1	11	78	68
-1	11	75	70
0	8	75	86
-3	10	69	59
2	3	70	-69
-1	14	67	63
3	6	67	70
0	14	67	-64
-2	4	65	78
-1	6	102	105
0	12	41	29
0	3	42	-44
1	5	43	-54
-2	7	45	-39
-4	6	47	-45
1	10	46	45
-3	2	51	43
-3	1	54	-53
0	7	19	45
-1	1	17	20
-2	3	34	-39
1	3	35	39
2	1	37	-34
0	4	13	-51
0	0	540	522
-1	7	382	369
1	4	94	-88
1	2	338	344
-1	12	106	-103
-1	4	281	-272
1	0	280	-271
-2	5	272	265
0	5	264	243
0	2	284	-252
0	6	237	-231
0	9	236	227
-1	3	191	188
2	4	163	160
-3	3	112	95
2	2	132	-130
0	1	137	133
1	7	136	130
1	1	141	-148
K = 3			
H	L	FO	FC
1	1	142	147
0	10	144	141
0	9	146	141
-1	1	147	171
0	1	156	144
-1	12	111	107
1	4	133	138
0	3	136	159
-2	10	112	110
2	0	132	-132
2	2	164	-170
1	7	173	-172
-2	6	182	181
-1	8	222	222
1	6	235	241
-2	5	205	211
-1	3	291	-264
-1	10	105	101
-1	7	259	252
0	5	337	-323
2	8	104	97
-1	2	349	356
1	0	344	-353
0	2	349	343
0	4	420	410
1	5	33	44
-2	8	53	46
1	11	53	46
-2	14	53	-47
1	8	51	-47
1	2	45	54
-1	5	42	46
0	6	42	-35
2	1	41	51
-2	3	40	37
-3	8	64	64
3	4	63	-58
-1	6	56	-49
2	3	68	83
2	9	71	-59
-1	14	71	-63
-2	1	73	-72
-2	4	74	-74
-3	2	79	-52
1	7	173	-172
-2	12	86	-91
1	3	86	76
0	12	83	80
-3	4	100	91
-2	7	99	103
-3	10	92	-84
-3	3	93	85
-1	9	99	106
K = 4			
H	L	FO	FC
-2	1	97	99
-1	2	95	99
0	1	95	93
0	5	93	100
-3	2	99	93
0	14	88	83
-1	3	137	134
2	4	125	-111
-1	4	125	135
1	0	121	-125
1	1	80	-92
2	2	78	-74
2	0	71	73
-3	8	71	61
-1	10	56	43
-3	5	58	54
0	8	62	54
-2	8	63	62
1	4	66	-67
-3	1	65	-53
2	1	44	-36
-1	1	44	39
0	4	48	59
1	7	55	50
0	6	37	49
1	5	34	40
1	2	410	-398
0	0	685	-656
0	7	318	-299
-1	5	322	-316
-2	2	107	112
0	2	107	-120
-2	4	177	183
-1	6	177	172
-2	3	171	-158
-1	14	120	118
-2	10	130	130
-2	12	161	155
1	9	143	-145
-3	10	139	127
-1	12	139	137
K = 5			
H	L	FO	FC
-2	4	161	-151
-1	10	139	-140
-2	2	138	-131
1	1	138	-146
-2	10	128	-132
1	5	132	-144
-1	12	131	-127
0	8	167	-158
0	12	114	-107
-2	8	109	-106
0	6	185	-174
2	2	191	188
-1	1	251	-248
0	4	252	-227
-1	3	244	-247
-1	6	221	-212
0	5	225	-231
-1	4	207	-207
0	1	214	-216
1	4	205	-192
0	3	312	-297
-1	2	283	-281
-2	1	104	-104
0	2	400	-394
1	0	388	383
0	9	27	-45
1	2	14	-23
3	4	52	45
1	12	44	-39
2	6	64	-66
-3	6	60	-59
1	6	58	-54
3	0	57	54
-1	5	67	-75
-1	8	61	-60
0	7	69	-59
0	10	81	-73
2	1	81	-80
1	3	125	-123
2	0	127	126
1	7	88	-88
1	8	99	-95
0	14	84	-77
1	10	83	-71
-2	5	85	-77
-1	7	93	-81
-3	2	91	-79
-3	8	94	-86
K = 6			
H	L	FO	FC
0	6	92	95
-1	4	90	102
-3	7	87	87
2	3	99	107
-2	13	85	89
-1	13	122	113
-1	3	117	120
2	7	80	75
1	7	76	80
-1	1	102	101
-3	5	72	67
0	9	58	64
1	8	55	52
1	3	55	63
2	4	103	98
3	1	63	-70
1	4	66	-63
-1	6	37	-41
-1	7	47	54
2	2	52	-60
-1	5	54	-63
-3	3	49	50
-2	5	50	53
-2	2	51	59
-1	12	51	-57
-3	6	21	20
2	5	35	32
0	8	462	434
-2	[illegible]	104	102
1	2	286	278
0	12	106	108
1	0	115	-114
-1	11	108	101
0	1	216	195
0	5	109	116
-2	7	113	126
-2	9	129	129
0	2	139	-125
-2	11	138	140
1	1	151	146
-1	9	144	147
-3	9	111	109
K = 7			
H	L	FO	FC
0	4	145	-157
0	6	146	-144
-1	5	143	-151
1	1	153	138
-2	8	150	-159
0	10	110	-104
2	2	162	154
-2	6	112	-115
-2	1	165	158
-1	4	169	-173
-1	13	171	-178
1	4	221	-215
0	8	224	206
0	12	127	-128
0	5	285	285
1	0	320	316
-1	3	313	307
0	2	389	-362
0	9	54	-50
3	4	54	55
-3	4	54	-52
2	3	48	38
1	9	45	38
2	0	45	37
-2	3	65	64
1	5	65	58
1	8	64	-67
-1	7	58	-58
0	3	55	61
2	1	73	-83
-2	10	67	-58
-1	12	81	-71
1	7	118	118
-1	2	117	-122
-1	5	116	108
-2	2	101	-107
3	3	59	-59
3	0	49	46
1	3	126	121
2	6	90	-88
0	7	93	89
1	6	97	-93
K = 8			
H	L	FO	FC
1	5	95	-93
-3	5	95	-90
-3	8	83	-85
-1	9	126	-138
0	8	79	83
-3	3	76	71
0	3	102	-104
-2	8	74	-71
0	11	76	-81
1	8	73	-84
0	9	71	72
-2	6	56	-59
2	5	56	-57
-2	12	58	-51
3	0	59	-57
-3	6	64	-60
1	10	65	63
2	3	65	64
2	0	45	-46
-1	6	45	43
-1	1	54	-53
2	7	53	-48
-1	2	50	-51
-1	5	49	51
0	0	474	476
1	0	28	-42
-1	7	116	109
1	2	353	341
-1	4	233	-240
-2	5	114	109
0	1	177	-184
0	6	187	-179
-2	10	149	-145
-1	12	154	-147
-2	2	161	-163
2	4	156	146
-2	7	128	-138
1	3	131	-135
1	1	131	129
K = 9			
H	L	FO	FC
0	8	128	123
-1	7	129	132
-1	6	135	133
-2	7	111	-121
0	5	144	-143
-1	2	193	202
0	4	198	204
1	6	105	107
-3	2	37	28
1	2	51	52
1	7	103	-110
1	1	46	43
-1	8	102	92
1	5	62	85
1	11	60	56
2	9	60	-65
0	2	58	59
-2	10	103	104
-2	1	68	-68
0	6	68	58
-2	2	60	56
1	0	69	-65
1	10	74	68
0	3	76	70
2	7	78	60
-2	5	123	125
-1	3	128	-127
-2	6	83	76
0	10	86	81
-1	12	91	96
-3	3	90	87
-1	9	95	-98
0	9	99	102
-1	6	94	84
-3	5	91	-87
K = 10			
H	L	FO	FC
-1	1	99	-99
-2	2	97	-94
1	5	96	-94
1	10	89	91
0	3	61	-125
0	5	122	123
-1	3	121	122
-2	5	127	125
1	7	73	66
-3	3	60	54
-2	1	61	60
2	7	58	-63
1	4	46	50
0	2	48	57
2	6	45	31
2	1	51	54
-1	6	264	262
-2	4	221	221
-3	2	114	119
0	6	195	-195
0	8	184	188
-1	7	176	176
1	8	166	-160
-1	4	150	-157
0	3	134	-125
0	9	131	137
K = 11			
H	L	FO	FC
1	1	130	135
0	1	134	138
0	9	159	166
1	3	111	109
1	7	147	-153
-2	5	191	190
-1	3	200	-197
-1	7	206	221
0	5	226	-227
-2	1	105	-99
2	1	53	58
0	3	61	68
-2	6	57	62
-2	2	58	58
2	2	55	-56
1	5	65	71
-1	1	64	71
1	0	63	-64
2	5	70	68
-2	3	69	58
-2	4	77	-69
2	3	94	92
-1	6	92	-74
K = 12			
H	L	FO	FC
-1	4	94	-109
1	8	90	-92
-2	3	83	-82
-1	5	120	-120
1	3	101	98
0	5	75	82
1	1	79	-68
-1	3	71	79
-2	2	63	-71
0	7	104	-108
1	7	51	53
2	5	51	49
-2	1	43	50
2	4	60	-86
0	6	116	-121
0	0	235	-239
0	4	206	-207
-1	2	195	-198
1	2	186	-178
0	2	195	-192
2	2	108	-104
1	0	175	-182
0	1	112	111
1	4	111	-103
1	6	134	-136
2	0	132	-123
K = 13			
H	L	FO	FC
0	1	129	134
1	3	121	119
-2	3	86	91
1	1	100	99
-1	5	89	91
2	0	86	76
-1	2	88	-85
K = 14			
H	L	FO	FC
0	0	94	101
-1	5	97	-103
1	3	65	57
0	1	66	62
0	5	57	-67
1	1	59	-50
1	2	74	77
0	2	45	48

Table 7. Final values of observed and calculated structure factors (X10)

Table 8. Least square equations of planes and deviations from planes[a]

---

1) Equation of least squares plane No. 1 for N1, C2, C3, C4, C5, C6, C7, O8, C9, C10, O11, and O12 $(0.8754)X + (-0.0517)Y + (0.4806)Z - (2.4557) = 0$

Atomic distances from plane (Å)

N1	0.004	O11	0.015
C2	-0.006	O12	-0.013
C3	-0.025	H1	0.09
C4	-0.010	H2	-0.65
C5	-0.002	H3	0.12
C6	0.017	H4	0.38
C7	0.023	H5	0.04
O8	-0.000	H6	-0.07
C9	-0.004	H7	-0.15
C10	0.003	H8	-0.12

2) Equation of least squares plane No. 2 for N1, C2, C3, C4, C5, C6, C7, O8 $(0.8769)X + (-0.0533)Y + (0.4776)Z - (2.4312) = 0$

Atomic distances from plane (Å)

N1	0.002	C7	0.020
C2	-0.010	O8	-0.005
C3	-0.020	H1	0.08
C4	-0.010	H5	0.04
C5	-0.003	H6	-0.05
C6	0.020	H7	-0.15

---

[a] The coordinate system used for the least squares planes was: $X = xa\sin\gamma + zc(\cos\beta - \cos\alpha\cos\gamma)/\sin\gamma$; $Y = xa\cos\gamma + by + cz\cos\alpha$; $Z = zv/ab\sin\gamma$.

Table 8 (continued)

3) Equation of least squares plane No. 3 for C9, C10, O11 and O12

$$(0.8695)X + (-0.0479)Y + (0.4916)Z - (2.5436) = 0$$

Atomic distances from plane (Å)

C9	-0.000	O12	-0.000
C10	0.001	H8	-0.1060
O11	-0.000		

4) Equation of least squares plane No. 4 for C9, C10, O11, O12, and H8

$$(0.8566)X + (-0.0616)Y + (0.5121)Z - (2.6628) = 0$$

Atomic distances from plane (Å)

C9	0.042	O12	0.010
C10	0.007	H8	-0.03
O11	-0.023		

Table 9. Selected internal distances and angles

Interatomic distances for Beta-picoline-N-oxide fumaric acid adduct

N1 --- C2	1.380 ± 0.007
C2 --- C3	1.365 ± 0.010
C3 --- C4	1.391 ± 0.010
C4 --- C5	1.382 ± 0.011
C5 --- C6	1.343 ± 0.010
N1 --- C6	1.345 ± 0.009
N1 --- 08	1.304 ± 0.006
C3 --- C7	1.564 ± 0.010
C6 --- 011	3.331 ± 0.008
011 --- C10	1.188 ± 0.008
C10 --- 012	1.332 ± 0.009
C10 --- C9	1.491 ± 0.010
012 --- 08	2.517 ± 0.006
C2 --- H1	1.216 ± 0.073
C7 --- H2	0.730 ± 0.084
C7 --- H3	1.272 ± 0.072
C7 --- H4	1.163 ± 0.073
C4 --- H5	1.095 ± 0.070
C5 --- H6	1.100 ± 0.070
C6 --- H7	0.849 ± 0.068
011 --- H7	2.511 ± 0.070
C9 --- H8	1.141 ± 0.072

Table 9 (continued)

Interatomic angles for Beta-picoline-N-oxide fumaric acid adduct

Atom (T-V-T)	Bond angle (°)
N1-C2-C3	118.38 ± 0.82
N1-C2-H1	114.79 ± 3.23
C3-C2-H1	126.54 ± 3.08
C3-C4-C5	115.30 ± 0.80
C2-C3-C7	115.73 ± 0.85
C2-C3-C4	123.11 ± 0.74
C3-C7-H2	96.16 ± 7.82
C3-C7-H3	100.05 ± 3.04
C3-C7-H4	87.45 ± 3.75
C3-C7-H5	121.72 ± 3.79
C3-C4-C5	115.30 ± 0.80
C5-C4-H5	122.65 ± 3.82
C4-C5-H6	110.45 ± 3.76
C6-C5-H6	127.37 ± 3.76
C5-C6-H7	131.77 ± 5.54
N1-C6-H7	104.44 ± 5.30
C6-N1-08	122.50 ± 0.58
C6-011-C10	114.20 ± 0.57
011-C10-012	124.00 ± 0.76
011-C10-C9	125.39 ± 0.80
012-C10-C9	110.60 ± 0.67
C10-012-08	122.42 ± 0.46
C6-H7-011	162.44 ± 7.07
N1-08-012	133.55 ± 0.42

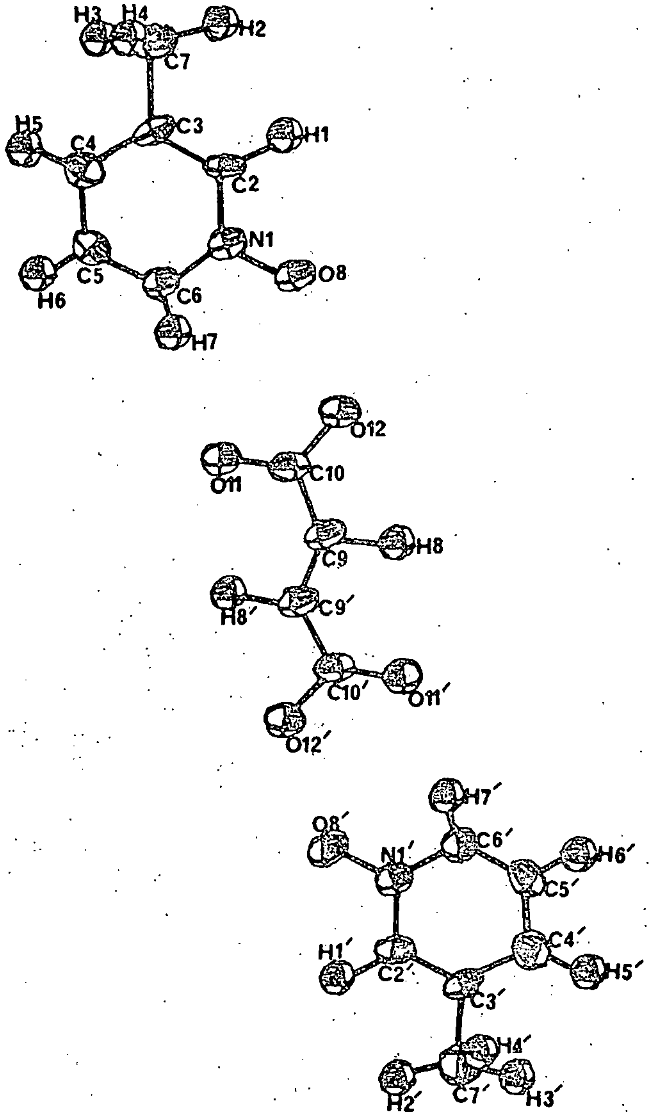

Figure 3. Beta-picoline-N-oxide fumaric acid adduct molecule

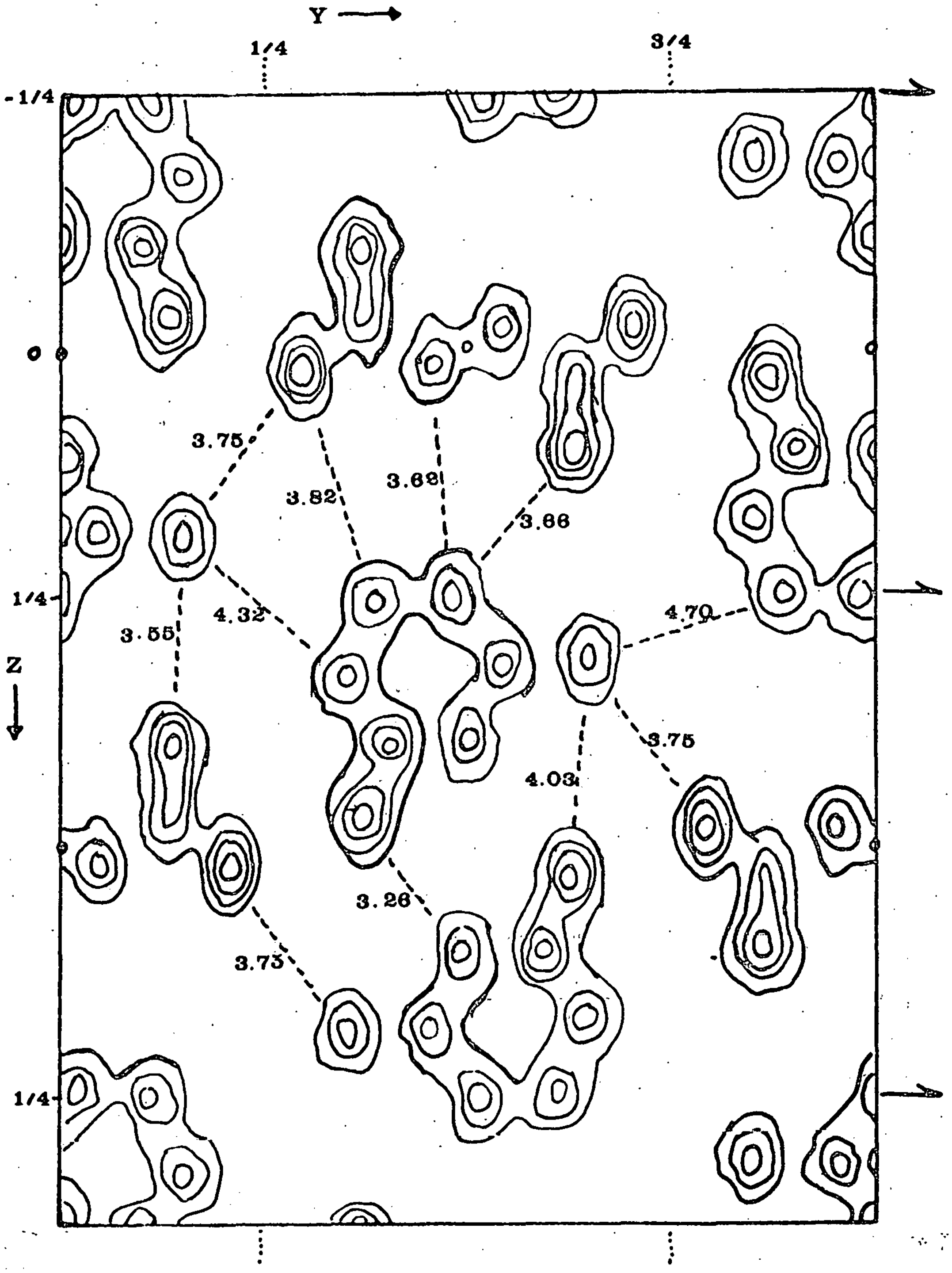

Figure 4. Electron density projection of APAB along a-axis

LITERATURE CITED

1. Lawton, S. L., and R. A. Jacobson, *Inorg. Chem.* *5*, 743 (1966).

2. Hubbard, C. R., and R. A. Jacobson, *Iowa Academy of Science*, *75*, 85 (1968).

3. Lawton, S. L., and R. A. Jacobson, *Inorg. Chem.* *7*, 2124 (1968).

4. Hackert, M. L., S. L. Lawton, and R. A. Jacobson, *Iowa Academy of Science*, *75*, 97 (1968).

5. Porter, S. K., and R. A. Jacobson, *J. Chem. Soc., Section A*, 1356 (1970).

6. Porter, S. K., and R. A. Jacobson, *J. Chem. Soc., Section A*, 1359 (1970).

7. Lawton, S. L., R. A. Jacobson, and R. S. Frye, *Inorg. Chem.*, *9*, 0000 (1970).

8. Clark, J. R., R. A. Jacobson, and R. G. Baughman, *Inorg. Chim. Acta*, *4*, 0000 (1970).

9. Williams, D. E., "LCR-2, A Fortran Lattice Constant Refinement Program," U.S. Atomic Energy Commission Report IS-1052 (Iowa State University and Institute for Atomic Research, Ames, Iowa). 1964.

10. Busing, W. R., K. O. Martin, and H. A. Levy, "OR FLS, A Fortran Crystallographic Least Squares Program," U.S. Atomic Energy Commission Report ORNL-TM-305 (Oak Ridge National Laboratory, Oak Ridge, Tennessee). 1962.

11. Doyle, R. A., and P. S. Turner, *Acta Cryst.* *A24*, 390 (1968).

12. Templeton, D. H. in "International Tables for X-ray Crystallography," Vol. III, The Kynock Press, Birmingham, England, 1962, pp. 215, 216, Table 3.3.2C.

13. Romers, C., and E. W. M. Keulemans, *Koninkl. Ned. Akad. Wetenschap., Proc.*, *B61*, 345 (1958).

14. Hackert, Marvin L., Robert A. Jacobson, and Timothy A. Keiderling, *Inorg. Chem.* *10*, 0000 (1971).

15. Gorres, Byron T. The crystal and molecular structure of the 2-amino-5-chloropyridine hydrochloride photodimer and the β-picoline-N-oxide fumaric acid adduct. Unpublished Ph.D. thesis. Princeton, New Jersey, Library, Princeton University. 1964.

16. Mighell, A. D., and R. A. Jacobson, *Acta Cryst*., *16*, 443 (1963).

17. Simpson, P. G., R. D. Dobrott, and W. N. Lipscomb, *Acta Cryst*., *18*, 169 (1965).

18. Hamilton, W. C., *Acta Cryst*., *18*, 866 (1965).

19. Gorres, B. T., and R. A. Johnson, *Acta Cryst*., *17*, 1599 (1964).

20. Mighell, A. D., and R. A. Jacobson, *Acta Cryst*., *17*, 1554 (1964).

21. Busing, W. R., K. O. Martin, H. A. Levy, C. R. Hubbard, and C. O. Quicksall, "OR FLS, A Fortran Crystallographic Least Squares Program," Modification of OR FLS to include a secondary extinction refinement parameter (Iowa State University and Institute of Atomic Research, Ames, Iowa). 1970.

22. Stewart, R. F., E. R. Davidson, and W. T. Simpson, *J. Chem. Phys*., *42*, 3175 (1965).

23. Hamilton, W. C., *Annual Review of Physical Chemistry*, *13*, 19 (1962).

24. Brown, C. J., *Acta Cryst*., *21*, 1 (1966).

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation and gratitude to:

Prof. Robert A. Jacobson for his helpful suggestions, thought provoking discussions, and continued interest in this work;

the Atomic Energy Commission and the State of Iowa for financial assistance in the form of research and teaching assistantships;

Jim Benson for his helpful comments and suggestions during the data collection process;

Fred Hollenbeck for his suggestions and technical assistance;

and to my deceased father, Frederick McAfee, whose prolonged interest and encouragement helped during my graduate study;

and to my devoted wife, Katy, for her moral and financial support during graduate school.