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The Crystal and Molecular Structure of the β-Picoline-*N*-oxide–Fumaric Acid Adduct*

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The crystal structure of the β-picoline-*N*-oxide–fumaric acid adduct, $2(C_6H_7NO) \cdot C_4H_4O_4$, has been determined by three-dimensional X-ray analysis. The crystals were monoclinic, space group $P2_1/c$, $a = 3.888 \pm 0.003$, $b = 14.194 \pm 0.010$, $c = 14.663 \pm 0.011$ Å, $\beta = 98.85 \pm 0.01°$, and $Z = 2$. The structure was solved by a symmetry-map frequency-check procedure in conjunction with a roving molecular fragment. A full-matrix weighted least-squares refinement modified to include a secondary extinction parameter gave a final conventional discrepancy index of $R = 0.052$ and a weighted discrepancy index of $wR = 0.037$ for 533 reflections $[I_N > 3\sigma(I)]$ recorded by a scintillation counter method. The β-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 β-picoline-*N*-oxide ring appears to hold the adduct together. This short $O \cdots O$ distance of 2.517 ± 0.006 Å lies within a range characteristic of a symmetric hydrogen bond.

Introduction

E. C. Taylor and R. O. Kan have found from colligative property measurements that a 2:1 adduct of β-picoline-*N*-oxide and fumaric acid can be prepared by refluxing stoichiometric ratios of the two in water. Their spectral studies [nuclear magnetic resonance, infrared and ultraviolet] of the adduct in solution indicated only a mixture of the two reactants. Since the adduct forms stable colorless crystals, we decided to undertake a crystal structure investigation to obtain more complete structural information about the nature of this adduct. The structure determination led to the development of a new method to determine structures containing a rigid group of atoms.

Experimental

Crystal data

β-Picoline-*N*-oxide–fumaric acid adduct, $C_{16}H_{18}N_2O_6$, F.W. 334·3, monoclinic, $P2_1/c$, $a = 3.888 \pm 0.003$, $b = 14.194 \pm 0.010$, $c = 14.663 \pm 0.011$ Å, $\beta = 98.85 \pm 0.10°$, $V = 799.9 \pm 1.1$ Å³, $d_{obs} = 1.36$ g ml⁻¹ (by flotation), $d_{calc} = 1.388$ g ml⁻¹ for $Z = 2$, $\mu = 1.14$ cm⁻¹, Mo $K\alpha$ ($\lambda = 0.71069$ Å), secondary extinction coefficient: 3824·4.

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: $0k0$ when $k = 2n + 1$ and $h0l$ when $l = 2n + 1$. These conditions uniquely specify 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 by the θ–2θ scan technique (2° min⁻¹) with backgrounds measured for 100 s at both ends of the scan. A crystal of approximate dimensions $0.24 \times 0.24 \times 0.36$ mm was mounted so that the (010) axis was coincident with the φ axis. All reflections having sin $\theta/\lambda < 0.538$ (45° in 2θ) were measured with Zr-filtered Mo $K\alpha$ 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, 533 had $I_N > 3\sigma(I)$ and were used for subsequent calculations.

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

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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 difficult to interpret and yielded no refinable 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 β-picoline-N-oxide ring. This eight-atom group was then moved over a symmetry map (Mighell & Jacobson, 1953; Simpson, Dobrott & Lipscomb, 1965; Hamilton, 1965). 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 β-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 map 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 use of the frequency-check procedure (Gorres & Jacobson, 1964). 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 index $[R = \sum(|F_o| - |F_c|)/\sum|F_o|]$ of 0·34. Refinement with isotropic thermal parameters immediately reduced this value to 0·13, using a weighting scheme described previously (Mighell & Jacobson, 1964), 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 with anisotropic temperature factors and the positional parameters of the eight hydrogen atoms were refined with a constant isotropic thermal parameter, B, of 3 Å². The calculated structure amplitudes were corrected for real and imaginary parts of anomalous dispersion due to the non-hydrogen atoms. The largest structure factors showed evidence of secondary extinction and a secondary extinction parameter (3824·4) was included in the refinement. The weights were checked by plotting $\overline{w\Delta^2}$ against $\sin\theta/\lambda$ and a small adjustment was subsequently made. The final values of R and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$ were 0·052 and 0·037, respectively.

The X-ray scattering factors of Doyle & Turner (1968) were used for the non-hydrogen atoms. For hydrogen, the contracted form of Stewart, Davidson & Simpson (1965) 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 1 and Table 2, respectively. In Table 3 are given the final values of the observed and calculated structure factors ($\times 10$).

Description of the structure

Fig. 1 illustrates the whole β-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 β-picoline-N-oxide ring. The O(8)$\cdots$O(12) distance is 2·517 ± 0·006 Å and the N(1)–O(8)$\cdots$O(12) angle is 133·5 ± 0·4°. The O(8)$\cdots$O(12) distance lies within the range that Hamilton (1962) would classify as a probably symmetrical hydrogen bond. However, it was just this hydrogen atom that could not be reliably located. There appeared to be some diffuse peaks around the oxygen
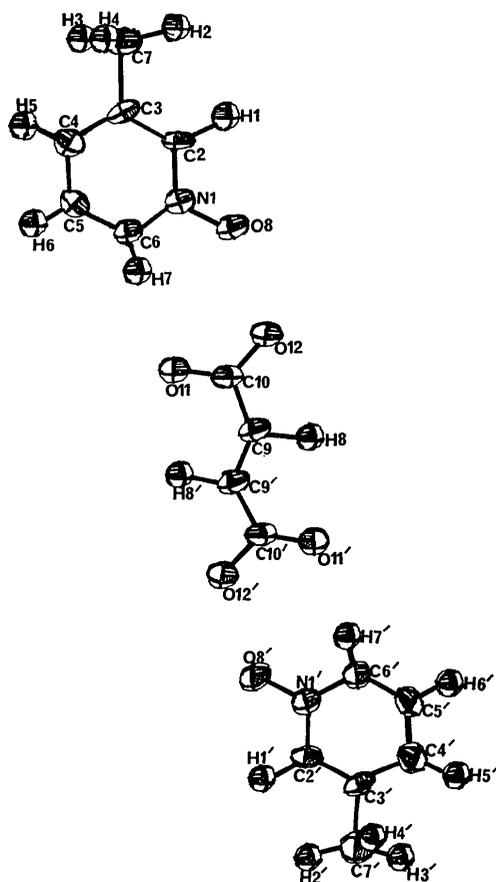

Fig. 1. β-Picoline-N-oxide–fumaric acid adduct molecule.

atoms 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.

Table 1. *Final positional parameters and estimated standard errors*

All nonhydrogen atom positional parameters are ×10⁴; all hydrogen atom positional parameters are ×10³.

	x	y	z
N(1)	2275 (17)	4047 (3)	3972 (4)
C(2)	2540 (21)	5014 (4)	3912 (6)
C(3)	3716 (21)	5388 (5)	3159 (5)
C(4)	4605 (24)	4841 (5)	2444 (6)
C(5)	4304 (21)	3879 (5)	2554 (5)
C(6)	3192 (24)	3503 (5)	3298 (6)
C(7)	4073 (2)	6485 (0)	3151 (0)
O(8)	1109 (15)	3698 (3)	4688 (3)
C(9)	−286 (22)	411 (4)	5171 (5)
C(10)	0605 (24)	1291 (5)	4704 (6)
O(11)	1696 (16)	1326 (3)	3990 (3)
O(12)	4 (17)	2046 (3)	5196 (4)
H(1)	194 (17)	544 (4)	485 (5)
H(2)	275 (25)	656 (6)	274 (6)
H(3)	319 (18)	668 (4)	393 (5)
H(4)	592 (18)	639 (5)	260 (5)
H(5)	544 (18)	511 (5)	191 (5)
H(6)	494 (17)	350 (4)	194 (5)
H(7)	237 (19)	296 (4)	339 (5)
H(8)	−158 (18)	45 (4)	581 (4)
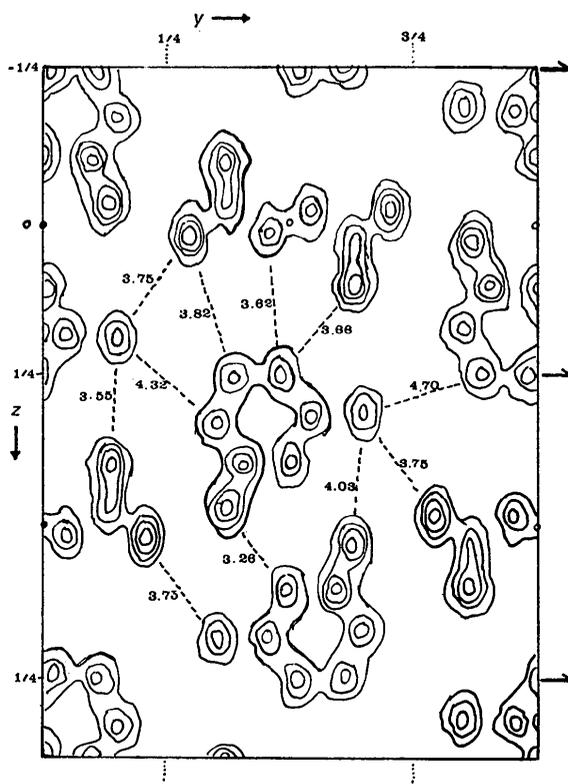
Fig. 2. Electron density projection along the *a* axis.

Table 2. *Final thermal parameters and estimated standard errors*

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

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
N(1)	934 (74)	33 (4)	50 (4)	−16 (13)	43 (15)	−28 (3)
C(2)	779 (89)	20 (4)	48 (5)	6 (14)	44 (17)	1 (3)
C(3)	663 (69)	31 (4)	48 (4)	−26 (16)	26 (14)	14 (4)
C(4)	915 (95)	40 (4)	55 (5)	19 (15)	62 (19)	−4 (4)
C(5)	1001 (93)	38 (4)	45 (5)	11 (1)	89 (18)	−8 (3)
C(6)	1227 (101)	25 (4)	52 (5)	−11 (17)	98 (19)	4 (4)
C(7)	1187 (138)	28 (4)	77 (7)	21 (19)	98 (23)	9 (5)
O(8)	1549 (73)	28 (2)	57 (3)	−13 (12)	159 (13)	5 (2)
C(9)	881 (81)	30 (4)	61 (5)	−30 (18)	87 (17)	5 (5)
C(10)	892 (87)	29 (4)	51 (5)	−38 (16)	32 (18)	1 (5)
O(11)	1575 (75)	30 (2)	57 (3)	−26 (12)	128 (14)	0 (3)
O(12)	1601 (72)	32 (3)	60 (3)	−26 (11)	158 (13)	−7 (2)

H(1)–H(8) have isotropic temperature factors fixed at 3·00 Å².

Table 3. *Final values of observed and calculated structure factors* (×10)

Table 4. *Least-squares planes and deviations* (Å)

The coordinate system used for the least-squares plane was:
$$X = xa + yc \cos \beta; \quad Y = by; \quad Z = yc \sin \beta.$$

(1) Equation of least-squares plane for N(1), C(2), C(3), C(4), C(5), C(6), C(7), O(8), C(9), C(10), O(11), and O(12): $(0.8754)X + (-0.0517)Y + (0.4806)Z - (2.4557) = 0$

N(1)	0.004	O(11)	0.015
C(2)	−0.006	O(12)	−0.013
C(3)	−0.025	H(1)	0.09
C(4)	−0.010	H(2)	−0.65
C(5)	−0.002	H(3)	0.12
C(6)	0.017	H(4)	0.38
C(7)	0.023	H(5)	0.04
O(8)	−0.000	H(6)	−0.07
C(9)	−0.004	H(7)	−0.15
C(10)	0.003	H(8)	−0.12

(2) Equation of least-squares plane for N(1), C(2), C(3), C(4), C(5), C(6), C(7), O(8): $(0.08796)X + (-0.0533)Y + (0.4776)Z - (2.4312) = 0$

N(1)	0.002	C(7)	0.020
C(2)	−0.010	O(8)	−0.005
C(3)	−0.020	H(1)	0.08
C(4)	−0.010	H(5)	0.04
C(5)	−0.003	H(6)	−0.05
C(6)	0.020	H(7)	−0.15

(3) Equation of least-squares plane for C(9), C(10), O(11) and O(12): $(0.8695)X + (-0.0479)Y + (0.4916)Z - (2.5436) = 0$

C(9)	−0.000	O(12)	−0.000
C(10)	0.001	H(8)	−0.1060
O(11)	−0.000		

Table 5. *Selected interatomic distances* (Å) *and angles* (°)

N(1)····C(2)	1.380 (7)	C(10)···C(9)	1.491 (10)
C(2)····C(3)	1.365 (10)	C(12)···O(8)	2.517 (6)
C(3)····C(4)	1.391 (10)	C(2)····H(1)	1.216 (73)
C(4)····C(5)	1.382 (11)	C(7)····H(2)	0.730 (84)
C(5)····C(6)	1.343 (10)	C(7)····H(3)	1.272 (72)
N(1)····C(6)	1.345 (9)	C(7)····H(4)	1.163 (73)
N(1)····O(8)	1.304 (6)	C(4)····H(5)	1.095 (70)
C(3)····C(7)	1.564 (10)	C(5)····H(6)	1.100 (70)
C(6)····O(11)	3.331 (8)	C(6)····H(7)	0.849 (68)
O(11)···C(10)	1.188 (8)	O(11)···H(7)	2.511 (70)
C(10)···O(12)	1.332 (9)	C(9)····H(8)	1.141 (72)
C(9)····C(9')	1.290 (14)		

N(1)–C(2)–C(3)	118.38 (0.82)
N(1)–C(2)–H(1)	114.79 (3.23)
C(3)–C(2)–H(1)	126.54 (3.08)
C(3)–C(4)–C(5)	115.30 (0.80)
C(2)–C(3)–C(7)	115.73 (0.85)
C(2)–C(3)–C(4)	123.11 (0.74)
C(3)–C(7)–H(2)	96.16 (7.82)
C(3)–C(7)–H(3)	100.05 (3.04)
C(3)–C(7)–H(4)	87.45 (3.75)
C(3)–C(7)–H(5)	121.72 (3.79)
C(3)–C(4)–H(5)	122.01 (3.82)
C(5)–C(4)–H(5)	122.65 (3.82)
C(4)—C(5)—H(6)	110.45 (3.76)
C(6)—H(5)—H(6)	127.37 (3.76)
C(5)—C(6)—H(7)	131.77 (5.54)
N(1)—C(6)—H(7)	104.44 (5.30)
C(6)—N(1)—O(8)	122.50 (0.58)
C(6)—O(11)—C(10)	114.20 (0.57)
O(11)–C(10)–O(12)	124.00 (0.76)
O(11)–C(10)–C(9)	125.39 (0.80)
O(12)–C(10)–C(9)	110.60 (0.67)
C(10)–O(12)–O(8)	122.42 (0.46)
C(6)—H(7)—O(11)	162.44 (7.07)
N(1)—O(8)—O(12)	133.55 (0.42)

The only other close contact for hydrogen bonding is between the C–H of the ε carbon to the other carboxyl oxygen of the fumaric acid. The O···H distance is 2.51 ± 0.07 Å (C–H···O angle is $162.4 \pm 7.0°$) and may be indicative of an additional weak hydrogen bond. Such a second hydrogen bond could account for all the nonhydrogen atoms of the adduct being within 0.02 Å of the least-squares plane (Table 4). The β-picoline-N-oxide and the fumaric acid moieties are planar to within 0.020 and 0.001 Å, respectively. All nonhydrogen 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 Fig. 2.

The internal distances and angles (Fig. 1 and Table 5) for the fumaric acid species appear to be consistent with the distances reported in the literature (Brown, 1966).

Conclusion

The adduct formed by fumaric acid and β-picoline-N-oxide has been shown to be held together by hydrogen-bonding forces and accounts 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, e.g., by neutron diffraction techniques, could provide useful information as to the presence or absence of a symmetrical hydrogen bond.

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