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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, $2(C_6H_7NO)$. $C_4H_4O_4$, has been determined by three-dimensional X-ray analysis. The crystals were monoclinic, space group $P2_1/c$, $a=3.888\pm0.003$, $b=14.194\pm0.010$, $c=14.663\pm0.011$ Å, $\beta=98.85\pm0.01^\circ$, 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···O distance of 2.517\pm0.006 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,

C₁₆H₁₈N₂O₆, F.W. 334·3, monoclinic, $P2_1/c$, $a=3\cdot888 \pm 0\cdot003$, $b=14\cdot194\pm0\cdot010$, $c=14\cdot663\pm0\cdot011$ Å, $\beta=98\cdot85\pm0\cdot10^\circ$, $V=799\cdot9\pm1\cdot1$ Å³, $d_{obs}=1\cdot36$ g ml⁻¹ (by flotation), $d_{calc}=1\cdot388$ g ml⁻¹ for Z=2, $\mu=1\cdot14$ cm⁻¹, Mo K α ($\lambda=0.71069$ 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: 0k0when 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 highorder 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 -2 θ 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 2 θ) were measured with 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, 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 eightatom 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



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

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 frequencycheck 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 nonhydrogen 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 nonhydrogen 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 $w\Delta^2$ against sin θ/λ and a small adjustment was subsequently made. The final values of R and $R_w =$ $(\sum w(|\dot{F}_{o}| - |\dot{F}_{c}|)^{2} / \sum w|F_{o}|^{2})^{1/2}$ 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)...O(12) distance is $2.517 \pm$ 0.006 Å and the N(1)-O(8)...O(12) angle is $133.5 \pm$ 0.4°. The O(8)...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 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 $\times 10^4$; all hydrogen atom positional parameters are $\times 10^3$.

	x	У	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)
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Fig. 2. Electron density projection along the a axis.

Table 2. Final the	ermal parameters and	d estimated standar	d errors
Anisotropic temperature f	$\operatorname{form} = \exp\left[-\left(\beta_{11}h^2 + \beta_2\right)\right]$	$_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2$	$2\beta_{13}hl+2\beta_{23}kl)].$

	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
					A .	

H(1)-H(8) have isotropic temperature factors fixed at 3.00 Å^2 .

Table 3. Final values of observed and calculated structure factors $(\times 10)$

K = 0 H L FD FC	-2 12 148 -159	3 4 73 -82	-3 1 54 -53	-2 6 182 181		-3 10 139 127	0 10 61 -73	2 5 35 32	1 9 45 38	2 0 45 -46	-2 10 103 104	0 8 184 188 0.5 15 82
-1 12 95 93	-2 13 112 119	1 8 81 -81				•1 12 139 137	2 1 81 -88	0 0 462 434	2 0 45 37	-1 6 45 43	-2 1 68 -68	•1 7 175 175 1 1 79 •58
-3 4 89 87	0 6 133 -145	-3 12 81 -78	-2 3 34 -19	-2 5 205 211	-2 1 97 99		1 1 125 -121	-2 1 104 102	-2 3 65 64	-1 1 24 -53	0 6 68 58	1 8 166 -160 -1 3 71 79
1 10 88 85	2 0 163 -106	1 6 79 83	1 3 35 39	-1 3 291 -264	-1 2 95 99	x • 5	1 7 88 -88	0 11 106 108	1 1 64 -67	-1 2 50 -51	1 0 69 -65	0 3 134 -125 0 7 104 -108
-1 6 86 83.	0 1 167 146	-2 3 124 -126	2 1 37 -34	-1 10 105 101	0 1 95 93	H L FO FC	1 8 99 -95	1 0 115 -114	-1 7 58 -58	-1 5 49 51	1 10 74 68	0 9 131 137 1 7 51 53
0 12 84 83	3 3 206 -203	1 1 122 120		•1 1 259 252	0 5 93 100	-2 4 101 -151	0 14 84 -77	-1 11 108 101	0 3 55 61	0 0 474 476	0 3 76 70	2 5 51 49
-6 6 83 -67	~3 10 114 -121	1 13 83 71	-1 7 382 369	2 8 104 97	0 14 88 83	-2 2 138 -131		0 5 109 116	-2 10 67 -54	-1 7 116 109	-2 4 123 125	K + 11 2 4 .43 -86
1 12 76 65	2 2 235 -243	0 13 85 -74	1 4 94 -88	-1 2 349 356	-1 3 137 134	1 1 130 -146	-1 7 93 -81	-2 7 113 126	-1 12 81 -71	1 2 353 341	-1 3 128 -127	H L FO FC 0 6 116-121
-2 8 69 66	0 2 350 352	-1 6 92 -99		1 0 344 -353	2 4 125 -111	-2 10 128 -132	-3 2 91 -79	-2 9 129 129	1 7 118 118	-1 4 233 -240	-2 4 63 76	1 1 130 135 0 0 235 -239
0 6 65 67	1 14 116 -119	-2 7 91 -94	-1 4 241 -212	0 4 420 430	1 0 121 -125	-1 12 131 -127	-3 8 94 -86	-2 11 139 -125	-1 2 117 -122	-2 5 114 109	0 10 86 81 a) 12 91 96	0 1 134 138 0 4 208 -207
-3 2 65 59	-1 2 343 341	-2 14 97 -94	1 0 200 -271	1 5 33 44	1 1 80 -92	0 8 167 -158		1 1 151 146	-2 2 101 -167	0 6 187 -179	-3 3 90 87	1 3 111 109 1 2 186 -178
1 8 57 36	-1 1 813 -835		-2 5 212 245	-2 8 53 46	2 2 78 -74	0 12 114 -107	K # 6	-1 9 144 147	3 3 39 -59	-2 10 149 -145	-1 9 95 -98	1 7 147 -153 0 2 195 -192
3 0 54 39	1 0 451 -463	K + 2	0 2 284 -252	-2 14 55 -47	-3 8 71 61	0 0 185 -176	N L FC FC	-3 9 111 109	3 0 49 46	-1 12 124 -147	-) 4 94 84	-1 3 200 -197 1 0 175 -182
2 2 51 38	2 1 452 -470	H L FO FC	0 6 237 -231	1 8 51 -47	-1 10 56 43	2 2 191 188	-1 4 90 102		2 6 90 -88	2 4 156 146	-3 5 91 -87	-1 7 206 221 0 1 112 111
2 4 643 653	0 10 27 15	-1 0 01 -09	-1 3 191 188	1 2 45 54	-3 5 50 54	-1 1 251 -248	-3 7 87 87	× • 1.	0 7 43 89	-2 7 128 -138		0 5 226 -227 1 4 111 -103
0 4 374 300	0 11 50 52	-2 2 126 -121	2 4 163 160	0 6 42 -35	-2 8 63 62	-1 3 266 -267	-2 13 44 107	A A 345 -157	1 6 47 -43	1 1 1 1 1 1 29	5 4 10	2 1 53 54 2 0 132 -123
-1 2 335 305	1 3 49 48	1 8 102 -97	-3 3 112 95	2 1 41 51	1 4 60 -07	-1 6 221 -212	-1 13 122 113	0 0 140 -144			H L FO FC	0 3 61 68
-2 10 297 -322	-3 9 47 -47	-2 12 116 -120	2 2 192 -190	-2 3 40 37	-3 1 65 -53	0 5 225 -231	-1 3 117 120	-1 0 143 -151	K = 8		-1 1 99 -99	-2 6 57 62 K • 13
0 2 290 246	0 14 44 36	0 13 71 62	1 7 136 130	3 4 63 -58	-1 1 44 39	0 1 214 -216	2 7 80 75	1 1 153 158	1 6 95 -93	N 1 FO FC	1 5 96 -96	7 7 55 -56 C 1 -129 136
-1 6 253 251	-3 • • 30	1 11 78 68	1 1 141 -148	-1 6 56 -49	0 4 48 59	1 4 205 -192	-1 1 102 101	0 10 110 -10+	-3 5 95 -90	0 8 128 123	1 10 89 91	1 5 65 71 1 3 121 119
1 4 212 200	0 8 34 -53	0 8 75 86		2 3 68 83	1 7 55 50	0 3 312 -297	-3 5 72 67	2 2 162 154	-3 8 83 -85	-1 7 129 132	0 3 61 -125	-1 1 64 71 -2 3 86 91
0 8 209 209	3 2 59 -45	-3 10 69 59	x • 3	-1 14 71 -63	1 5 35 40	-1 2 283 -281		-2 6 112 -115	-1 9 126 -135	-1 6 135 135	-1 1 121 122	2 5 70 68 -1 5 89 91
-1 8 196 195	-3 1 65 -61	2 3 70 -69	H L FO FC	-2 2 73 -72	1 2 410 - 398	0 2 400 - 394	1 3 55 63	-1 4 169 -173	-3 3 76 71	0 5 144 -143	-2 5 127 125	-2 3 69 58 2 0 86 76
-3 8 178 -176	-1 13 42 -55	3 6 67 70	6 10 144 141	-2 4 76 -74	0 0 405 -656	1 0 344 383	2 . 103 98	-1 13 171 -178	0 3 102 -104	-1 2 193 202	1 7 73 60	-2 4 77 -40 -1 2 88 -85
-2 0 163 160	-3 8 62 49	0 14 67 -64	0 9 146 141	1 7 173 -172	-1 5 322 -316	1 2 14 -21	3 1 65 -70	0 1 226 206	0 11 74 -81	1 6 105 107	-2 1 61 60	-1 6 92 -74 . * 14
-2 - 160 148	2 7 . 65 -59	-2 4 65 78	-1 1 147 171	-2 12 80 -91	-2 2 107 112	3 4 52 65	-1 6 37 -41	0 12 127 -128	1 8 73 -84	-3 2 37 28	2 7 58 -43	H L FO FC
0 10 145 137	0 7 69 -77	0 12 41 29	-1 12 111 107	0 12 83 80	0 2 107 -120	1 12 44 -39	-1 7 6 56	0 5 285 285	0 9 71 72	1 2 51 52	1 4 46 50	
	0 9 69 -55	0 3 42 -44	3 4 133 130	-3 4 100 91	-1 6 177 172	-3 6 60 -59	-1 5 54 -63	-1 3 313 307	2 5 56 -57	1 1 46 43	2 6 45 31	H L FO FC 1 3 45 57
	-3 5 68 -63	1 5 43 -54	0 3 136 159	-2 7 99 103	-2 3 171 -158	1 6 58 -54	-3 3 49 50	0 2 389 -362	-2 12 58 -51	-1 8 102 92	2 1 51 54	-1 4 94 -109 0 1 66 62
H L FO FC	-2 11 72 -67		2 0 132 -132	-3 10 12 -84	-1 14 128 118	3 0 57 54	-2 5 50 53	0 9 54 -50	3 0 59 -57	1 5 62 85	-1 6 264, 262	1 8 90 -92 0 5 57 -67
-2 9 145 -136	-2 10 75 66	1 10 40 45	2 2 104 -170	-1 9 49 106	-2 12 161 155	-1 8 01 -08	-1 12 51 -57		1 10 65 63	2 9 60 -65	-3 2 114 119	-1 5 120 -120 1 2 74 77
-1 > 143 -153	1 4 76 80	-3 2 51 43	1 7 173 -172		1 9 143 -145	0 7 69 -59	-3 6 21 20	2 3 48 38	2 3 65 64	0 2 58 59	0 6 195 -195	1 3 101 98 0 2 45 48

Table 4. Least-squares planes and deviations (A) The coordinate system used for the least-squares plane was: $X=xa+yc\cos\beta; Y=by; Z=yc\sin\beta.$

(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

/J+)A (0 0 0 1 /) 1	(0+000) $(2+557) = (2+557)$	0
N(1)	0.004	O(11) 0.012	
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)	-0.005	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) = 0C(9) -0.000 O(12) -0.000C(10) 0.001 H(8) -0.1060O(11) -0.000

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

$N(1) \cdots C(2)$	1.380 (7)	$C(10) \cdots C(9)$	1.491 (10)
$C(2) \cdots C(3)$	1.365 (10)	$C(12) \cdots O(8)$	2.517 (6)
$C(3) \cdots C(4)$	1.391 (10)	$C(2) \cdots H(1)$	1.216 (73)
$C(4) \cdots C(5)$	1.382 (11)	$C(7) \cdots H(2)$	0.730 (84)
$C(5) \cdots C(6)$	1.343 (10)	$C(7) \cdots H(3)$	1.272 (72)
$N(1) \cdots C(6)$	1.345 (9)	$C(7) \cdots H(4)$	1.163 (73)
$N(1) \cdots O(8)$	1.304 (6)	$C(4) \cdots H(5)$	1.095 (70)
$C(3) \cdots C(7)$	1.564 (10)	$C(5) \cdots H(6)$	1.100 (70)
$C(6) \cdots O(11)$	3.331 (8)	$C(6) \cdots H(7)$	0.849 (68)
$O(11) \cdots C(10)$	1.188 (8)	$O(11) \cdots H(7)$	2.511 (70)
$C(10) \cdots O(12)$	1.332 (9)	$C(9) \cdots H(8)$	1.141 (72)
$\mathbf{C}(9)\cdots\mathbf{C}(9')$	1.290 (14)		()
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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)C(11)-C(10)	114.20 (0.57)
O(11)-C(10)-O(12)	1 2 4·00 (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 $O \cdots H$ distance is 2.51 ± 0.07 Å (C-H···O angle is $162.4 \pm 7.0^{\circ}$) 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 frequencycheck 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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