Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(2)	1.362 (3)	O(1)—C(14)	1.454 (3)
C(2)—C(3)	1.403 (3)	C(2)—C(11)	1.366 (3)
C(3)—C(4)	1.365 (3)	C(4)—C(5)	1.411 (3)
C(5)—C(6)	1.412 (3)	C(5)—C(10)	1.410 (3)
C(6)—C(7)	1.363 (4)	C(7)—C(8)	1.397 (4)
C(8)—C(9)	1.362 (4)	C(9)—C(10)	1.410 (3)
C(10)—C(11)	1.425 (3)	C(11)—N(12)	1.416 (3)
N(12)—C(13)	1.267 (3)	C(13)—C(14)	1.504 (4)
C(14)—N(15)	1.436 (3)	C(14)—C(22)	1.548 (3)
N(15)—C(16)	1.414 (3)	N(15)—C(23)	1.442 (4)
C(16)—C(17)	1.375 (3)	C(16)—C(21)	1.366 (3)
C(17)—C(18)	1.369 (4)	C(18)—C(19)	1.366 (4)
C(19)—C(20)	1.388 (4)	C(20)—C(21)	1.387 (3)
C(21)—C(22)	1.503 (3)	C(22)—C(24)	1.521 (3)
C(22)—C(25)	1.551 (3)		

C(2)—O(1)—C(14)	119.2 (2)	O(1)—C(2)—C(11)	122.2 (2)
O(1)—C(2)—C(3)	117.0 (2)	C(3)—C(2)—C(11)	120.8 (2)
C(2)—C(3)—C(4)	119.7 (2)	C(3)—C(4)—C(5)	121.1 (2)
C(4)—C(5)—C(10)	119.4 (2)	C(4)—C(5)—C(6)	121.8 (2)
C(6)—C(5)—C(10)	118.8 (2)	C(5)—C(6)—C(7)	120.8 (2)
C(6)—C(7)—C(8)	119.9 (3)	C(7)—C(8)—C(9)	121.1 (2)
C(8)—C(9)—C(10)	120.1 (2)	C(5)—C(10)—C(9)	119.2 (2)
C(9)—C(10)—C(11)	122.4 (2)	C(5)—C(10)—C(11)	118.3 (2)
C(2)—C(11)—C(10)	120.6 (2)	C(10)—C(11)—N(12)	118.6 (2)
C(2)—C(11)—N(12)	120.7 (2)	C(11)—N(12)—C(13)	117.4 (2)
N(12)—C(13)—C(14)	126.7 (2)	O(1)—C(14)—C(13)	110.6 (2)
C(13)—C(14)—C(22)	115.5 (2)	C(13)—C(14)—N(15)	110.4 (2)
O(1)—C(14)—C(22)	109.6 (2)	O(1)—C(14)—N(15)	106.9 (2)
N(15)—C(14)—C(22)	103.3 (2)	C(14)—N(15)—C(23)	120.3 (2)
C(14)—N(15)—C(16)	108.0 (2)	C(16)—N(15)—C(23)	120.7 (2)
N(15)—C(16)—C(21)	109.5 (2)	N(15)—C(16)—C(17)	128.2 (2)
C(17)—C(16)—C(21)	122.3 (2)	C(16)—C(17)—C(18)	117.6 (2)
C(17)—C(18)—C(19)	121.3 (3)	C(18)—C(19)—C(20)	121.0 (3)
C(19)—C(20)—C(21)	117.9 (2)	C(16)—C(21)—C(20)	119.9 (2)
C(20)—C(21)—C(22)	130.5 (2)	C(16)—C(21)—C(22)	109.4 (2)
C(14)—C(22)—C(21)	100.7 (2)	C(21)—C(22)—C(25)	108.1 (2)
C(21)—C(22)—C(24)	115.7 (2)	C(14)—C(22)—C(25)	109.9 (2)
C(14)—C(22)—C(24)	112.8 (2)	C(24)—C(22)—C(25)	109.4 (2)

replacement of C(6) by an N atom does not alter the geometry of the spiro system; the slower ring-closure kinetics observed for the merocyanine form of the pyridobenzoxazine (Malatesta, 1991) presumably arises from a change in electronic structure.

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Acta Cryst. (1991). C**47**, 2569–2572

Structure of β-Ammoniumpropionitrile Hemifumarate

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(*Received* 4 *March* 1991; *accepted* 11 *April* 1991)

Abstract. 2-Cyanoethylammonium hemifumarate, $C_3H_7N_2^+.\frac{1}{2}C_4H_2O_4^{2-}$, $M_r = 128.12$, monoclinic, $P2_1/n$, $a = 5.163$ (2), $b = 23.472$ (13), $c = 5.458$ (3) Å, $\beta = 97.08$ (4)°, $V = 656.4$ Å^3, $Z = 4$, $D_x = 1.296$ g cm^{-3}, λ(Cu $K\alpha$) = 1.54179 Å, $\mu = 8.19$ cm^{-1}, $F(000) = 272$, $T = 293$ K, $R = 0.0534$ for 860 independent data. The crystal structure shows layers of β-ammoniumpropionitrile held together by antiparallel stacking of the nitrile groups, alternating with layers of fumarate dianions whose carboxyl groups form

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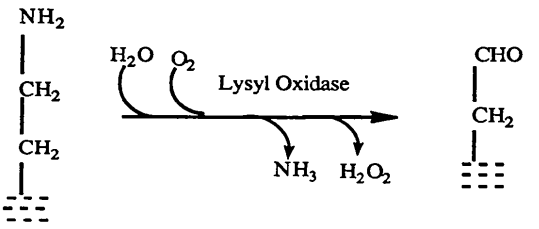
0108-2701/91/122569-04$03.00

bridging ion pairs with the ammonium groups of the cations.

Introduction. The condition of lathyrism, which often results in curvature of the spine or rupture of the aorta, occurs in animals when they ingest the seeds of the common sweetpea, *Lathyris odoratus*. The active agent has been shown to be a decarboxylated derivative of alanine, β-aminopropionitrile (BAPN). The condition is characterized biochemically by the fact that the collagen and elastin of lathyrism sufferers are abnormal in that the molecules are not properly cross-linked and they contain higher than normal concentrations of lysine. Since the cross-links derive from the condensation of lysine residues with nearby aldehyde groups, lathyrism must arise from some defect in either the generation of the aldehyde or in the condensation process. In fact, Pinnell & Martin (1968) showed that the enzyme lysyl oxidase, which generates the aldehyde involved in cross-linking according to the scheme below, is readily and irreversibly inhibited by BAPN.



Indeed, BAPN is used therapeutically to control fibrosis (or the generation of scar tissue) although, since the inhibition of lysyl oxidase leads to a weaker tissue, the dose rate is critical. The various aspects of lysyl oxidase, its mechanism and properties, have been reviewed by Kagan (1986). A mechanism for the inhibition by BAPN involving a covalent product has been proposed by Tang, Trackman & Kagan (1983). As part of a study of the enzyme, which has recently been found to contain the coenzyme PQQ or pyrroloquinolinequinone reviewed by Gallop, Paz, Flückiger & Kagan (1989), and its interaction with collagen, we have determined the crystal structure of the fumarate salt of protonated BAPN, β-ammoniumpropionitrile.

Experimental. The hemifumarate salt of β-ammoniumpropionitrile was obtained from Sigma Chemicals Ltd (Catalogue No. A3134), and recrystallized from water. *h0l* and *h1l* Weissenberg photographs of a crystal showed systematic absences consistent with the space group $P2_1/n$ and this was confirmed by examination of the $0k0$ reflections in the three-dimensional data set. Unit-cell dimensions were determined from 14 reflections in the range $35.8 \leq 2\theta \leq 48.4°$ measured at $\pm\omega$ on a Siemens AED-2 four-circle diffractometer with graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.54179$ Å). Corrections for Lorenz and polarization effects, and absorption by the semi-empirical method of North, Phillips & Mathews (1968), were applied. The reflections were merged to give 869 unique data with $I > 3\sigma(I)$ and $R_{merge} = 0.069$. Direct methods (Sheldrick, 1986) revealed all non-H atoms and hydrogens were added in their expected positions. Refinement, based on F, proceeded smoothly but required the C—H and N—H bond lengths, but not their isotropic temperature factors, to be restrained. All non-H atoms were refined anisotropically. Nine low-angle reflections with $F_o \ll F_c$ were deemed to suffer from extinction effects and were omitted from the refinement. The atomic scattering factors used were from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101). The programs used were *SHELX*76 (Sheldrick, 1976) and *SHELX*86 (Sheldrick, 1986). Table 1* summarizes the data collection and structure refinement with Table 2 containing the final refined coordinates. *CALC* (Gould & Taylor, 1983) was used to provide the molecular-geometry data presented in Tables 3 and 4. Diagrams were prepared using an interactive version of *ORTEP* (Johnson, 1965; Mallinson & Muir, 1985).

Discussion. Fig. 1 shows a diagram of the asymmetric unit. The structure has typical bond lengths and angles with torsion angles about C2—C3 and C3—N3 which indicate a fully staggered conformation. The angle N1—C1—C2 is effectively 180°. The fumarate anion is planar with an r.m.s. deviation of 0.045 Å for atoms O41, O42, C4, C5 and C5′ while that for the plane fitted through atoms N1, C1, C2, C3, N3 has a value of 0.032 Å. All three protons of the quaternary ion form hydrogen bonds with neighbouring carboxylates, producing a network summarized in Table 4. Whilst the hydrogen bonding in the *a* direction involves bifurcated bonds, that in the *c* direction involves a single bond and it is notable that H303 has the least satisfactory temperature factor with the C4—O41 bond being slightly shorter than that for C4—O42. The other stabilizing interaction in the crystal is that involving the antiparallel stacking of the nitrile groups, which run parallel to the *b* axis, with N1···C1, N1···C2 and C1···C1 distances of 3.378 (6), 3.411 (6) and 3.595 (6) Å respectively, and angles C1—N1···C1′ and N1···C1′—C2′ are 90.0 (3) and 76.3 (3)°

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54155 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Details of data collection and structure refinement*

Molecular formula	$C_3H_7N_2^+ . \frac{1}{2}C_4H_2O_4^{2-}$
Molar mass	128.12
Crystal dimensions (mm)	0.95 × 0.35 × 0.15
Crystal shape	Plate
Crystal system	Monoclinic
Space group	$P2_1/n$ (Alt. $P2_1/c$; No. 14)
Temperature (K)	293
Diffractometer used	Siemens–Stoë AED-2
Reflections to determine lattice parameters	14
Cell dimensions a (Å)	5.163 (2)
b (Å)	23.472 (13)
c (Å)	5.458 (3)
β (°)	97.08 (4)
Cell volume (Å^3)	656.4
Z	4
D_x (g cm^{-3})	1.296
$F(000)$	272
Radiation used (graphite monochromator)	Cu $K\alpha$
Linear absorption coefficient (cm^{-1})	8.19
Min. and max. transmission coefficients	0.3954, 0.6376
Max. $\sin\theta/\lambda$ (Å^{-1})	0.562
hkl range h	$-6 \rightarrow 6$
k	$-26 \rightarrow 26$
l	$0 \rightarrow 6$
Drift correction range (3 standard reflections)	1.000, 1.092
Reflections measured	2053
Reflections used in refinement	860
Parameters refined	116
Final R	0.0534
Final wR	0.0571
S	0.613
Weighting scheme from *SHELX*76	Unit weights
Maximum shift/e.s.d. on final cycle	0.005
Final difference Fourier (e Å^{-3}) max.	0.08
min.	−0.09

Table 2. *Fractional coordinates, with standard deviations in parentheses*

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j .$$

	x	y	z	U_{eq}
N1	0.0267 (9)	0.78228 (15)	0.5142 (8)	0.099 (3)
C1	0.0040 (8)	0.73423 (18)	0.4997 (8)	0.069 (3)
C2	−0.0297 (8)	0.67255 (16)	0.4806 (9)	0.065 (3)
C3	0.2254 (7)	0.64112 (15)	0.5117 (7)	0.0504 (21)
N3	0.1755 (5)	0.57952 (11)	0.4687 (5)	0.0410 (16)
O41	0.0465 (4)	0.42362 (9)	0.0163 (4)	0.0470 (14)
O42	0.2958 (4)	0.45391 (9)	0.3495 (4)	0.0463 (14)
C4	0.2400 (6)	0.45094 (12)	0.1168 (5)	0.0356 (18)
C5	0.4078 (6)	0.48187 (13)	−0.0421 (5)	0.0356 (17)
H21	−0.149 (8)	0.6574 (19)	0.617 (7)	0.116 (18)*
H22	−0.138 (7)	0.6610 (18)	0.308 (5)	0.098 (15)*
H31	0.324 (7)	0.6478 (17)	0.692 (4)	0.090 (14)*
H32	0.355 (6)	0.6540 (15)	0.382 (6)	0.073 (12)*
H301	0.045 (7)	0.5669 (18)	0.594 (7)	0.099 (15)*
H302	0.351 (5)	0.5575 (14)	0.530 (7)	0.075 (12)*
H303	0.126 (13)	0.567 (3)	0.282 (5)	0.196 (29)*
H5	0.382 (7)	0.4737 (14)	−0.232 (4)	0.068 (11)*

* Refined isotropically.

Table 3. *Bond lengths* (Å), *angles* (°) *and torsion angles* (°), *with standard deviations in parentheses*

N1—C1	1.136 (6)	N3—H301	1.059 (38)
C1—C2	1.460 (6)	N3—H302	1.060 (32)
C2—H21	1.083 (42)	N3—H303	1.061 (55)
C2—H22	1.067 (36)	O41—C4	1.255 (4)
C2—C3	1.501 (5)	O42—C4	1.269 (4)
C3—H31	1.063 (34)	C4—C5	1.488 (4)
C3—H32	1.074 (33)	C5—H5	1.045 (30)
C3—N3	1.482 (5)	C5—C5′	1.317 (4)*

N1—C1—C2	179.1 (0.5)	C3—N3—H301	106.6 (2.1)
C1—C2—H21	110.5 (2.2)	C3—N3—H302	107.6 (1.7)
C1—C2—H22	111.0 (2.0)	C3—N3—H303	115.7 (3.0)
C1—C2—C3	112.6 (0.4)	H301—N3—H302	104.4 (2.7)
H21—C2—H22	104.1 (3.0)	H301—N3—H303	116.4 (3.6)
H21—C2—C3	109.0 (2.2)	H302—N3—H303	105.4 (3.4)
H22—C2—C3	109.3 (2.0)	O41—C4—O42	122.4 (0.3)
C2—C3—H31	110.2 (1.9)	O41—C4—C5	118.9 (0.3)
C2—C3—H32	113.3 (1.8)	O42—C4—C5	118.7 (0.3)
C2—C3—N3	109.2 (0.3)	C4—C5—H5	118.4 (1.6)
H31—C3—H32	107.6 (2.5)	C4—C5—C5′	124.1 (0.3)
H31—C3—N3	110.2 (1.8)	H5—C5—C5′	117.5 (1.7)
H32—C3—N3	106.3 (1.8)		

C1—C2—C3—N3	−175.2 (0.3)
O41—C4—C5—C5′	170.0 (0.3)
O42—C4—C5—C5′	−8.9 (0.4)

* C5′ related to C5 by $1-x, 1-y, -z$.

Table 4. *Geometry around hydrogen bonds* (*distances in* Å, *angles in* °)

N3—O41	(*a*)	2.753 (4)	O41—H303	(*a*)	1.77 (5)
N3—O42	(*b*)	2.895 (4)	O42—H302	(*b*)	1.88 (3)
N3—O42	(*c*)	2.849 (4)	O42—H301	(*c*)	1.89 (4)

C3—N3—O41	(*a*)	102.8 (2)	N3—O41—C4	(*a*)	130.4 (2)
C3—N3—O42	(*b*)	94.1 (2)	N3—O42—C4	(*b*)	114.6 (2)
C3—N3—O42	(*c*)	110.7 (2)	N3—O42—C4	(*c*)	103.6 (2)

N3—H303—O41	(*a*)	152.5 (4.6)
N3—H302—O42	(*b*)	158.9 (2.6)
N3—H301—O42	(*c*)	149.2 (3.1)

Symmetry code: (*a*) $-x, 1-y, -z$; (*b*) $1-x, 1-y, 1-z$; (*c*) $-x, 1-y, 1-z$.

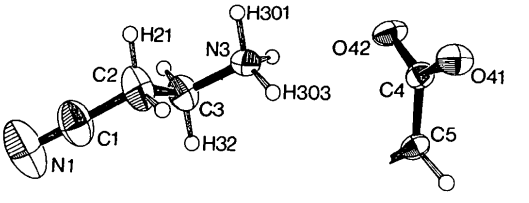


Fig. 1. β-Ammoniumpropionitrile hemifumarate. Non-H atoms are shown as 50% probability thermal ellipsoids. The fumarate lies on a centre of symmetry.

The biological activity of BAPN and its salt do not alter appreciably when the fumarate counter ion is replaced by chloride. Consequently, the active site of lysyl oxidase must be complementary to both the cationic and neutral forms of BAPN. This is consistent with the proposed mechanism of Tang *et al.* (1983) who suggest that it is the amino form which is responsible for the inhibitory effect. Confirmation of this will require the structure determination of the enzyme and to this end, crystallization trials on material prepared in Edinburgh (Shackleton & Hulmes, 1990) are in progress.

The authors thank Professor A. Miller and Drs R. O. Gould, D. J. S. Hulmes, D. R. Shackleton and P. Taylor for helpful discussions, and the SERC for financial support.

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Acta Cryst. (1991). C**47**, 2572–2575

Structure du *cis*-Dichloro-1,3 Tétramorpholinocyclotriphosphazène: $N_3P_3Cl_2(NC_4H_8O)_4$

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(*Reçu le* 11 *janvier* 1991, *accepté le* 8 *mai* 1991)

Abstract. $C_{16}H_{32}Cl_2N_7O_4P_3$, $M_r = 550{\cdot}31$, monoclinic, $P2_1/n$, $a = 9{\cdot}204\ (4)$, $b = 17{\cdot}100\ (4)$, $c = 16{\cdot}747\ (5)$ Å, $\beta = 103{\cdot}44\ (2)°$, $V = 2564\ (2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}47\ (1)$, $D_x = 1{\cdot}43$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ(Mo $K\alpha$) = 4·19 mm^{-1}, $F(000) = 1152$, $T = 298$ K, $R = 0{\cdot}050$ for 2126 independent reflections. The phosphazene ring runs parallel to $y0z$ and is aligned so as to form a plane parallel to $x0y$. The phosphazene ring is not perfectly planar and the morpholino groups are in the chair conformation. The Cl atoms have a *cis* disposition.

Introduction. L'étude structurale du *cis*-dichloro-1,3 tétramorpholinocyclotriphosphazène, composé particulièrement stable, a pour but de prévoir le mécanisme de polymérisation et l'arrangement dans l'espace résultant de la substitution des atomes de chlore par une diamine.

0108-2701/91/122572-04$03.00