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Structures of Nicotine Monomethyl Iodide and Nicotine Monohydrogen Iodide

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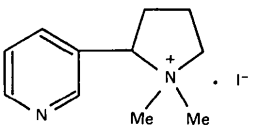
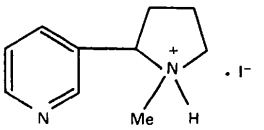
Abstract. 1,1-Dimethyl-2-(3-pyridyl)pyrrolidinium iodide, (I) $C_{11}H_{17}N_2^+.I^-$, $M_r=304{\cdot}2$, monoclinic, $P2_1$, $a=13{\cdot}972$ (3), $b=8{\cdot}389$ (1), $c=10{\cdot}739$ (3) Å, $\beta=96{\cdot}62$ (2)°, $U=1250{\cdot}2$ (4) Å^3, $Z=4$, $D_x=1{\cdot}62$ g cm^{-3}, Mo $K\alpha$, $\lambda=0{\cdot}71069$ Å, $\mu=25{\cdot}0$ cm^{-1}, $F(000)=600$, $T=293$ K, $R(wR)=0{\cdot}022$ (0·026) for 2310 reflections. 1-Methyl-2-(3-pyridyl)-1*H*-pyrrolidinium iodide, (II) $C_{10}H_{15}N_2^+.I^-$, $M_r=290{\cdot}1$, orthorhombic, $P2_12_12_1$, $a=13{\cdot}705$ (2), $b=9{\cdot}974$ (1), $c=8{\cdot}436$ (1) Å, $U=1153{\cdot}2$ (2) Å^3, $Z=4$, $D_x=1{\cdot}68$ g cm^{-3}, $\mu=27{\cdot}1$ cm^{-1}, $F(000)=568$, $T=200$ K, $R(wR)=0{\cdot}018$ (0·019) for 1818 reflections. The pyridine rings are planar and the pyrrolidine rings are folded. The additional methyl group in (I) is axial. The intramolecular separation of the two nitrogen atoms in nicotine monomethyl iodide [(I), 4·67 (1) Å] is less than in the monohydrogen iodide [(II), 4·740 (5) Å] and the dihydrogen iodide (4·96 Å). A comparison of the three structures is made with reference to their biological activity.

Introduction. The use of the terms 'muscarinic' and 'nicotinic' to describe different types of acetylcholine receptor originates from the observation by Dale (1914) that the lowering of blood pressure produced by small doses of acetylcholine was imitated by (+)-muscarine whereas the rise in blood pressure produced by high doses was imitated by (−)-nicotine. There is some structural resemblance between muscarine and acetylcholine; both contain a trimethylammonium group, but a resemblance between nicotine and acetylcholine is not easy to see. Nicotine is a ditertiary base (see formulae below) with pK_a's of 3·10 and 8·01 at 298 K (Barlow & Hamilton, 1962*a*); nicotine monomethyl iodide, in which the pyrrolidine ring is quaternized, has similar pressor activity to (−)-nicotine (Barlow & Dobson, 1955). It is more active than (−)-nicotine at the neuromuscular junction and it appears that it is the monoprotonated form of nicotine which is active (Barlow & Hamilton, 1962*a*). The structure of nicotine monomethyl iodide is therefore of biological interest, but it is also of interest because molecular models suggest that rotation about the bond between the pyridine and pyrrolidine rings may be sterically restricted (Barlow & Hamilton, 1962*b*).

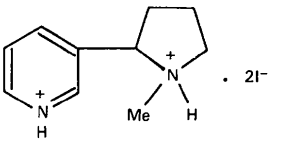
The structure of nicotine monomethyl iodide has therefore been investigated together with that of (−)-nicotine monohydrogen iodide. The latter should be biologically more appropriate than (−)-nicotine dihydrogen iodide, whose crystal structure was studied by Koo & Kim (1965) because the diprotonated form is not present to any appreciable extent at biological pH (7·6). It is also more appropriate for assessing possible steric effects, because in the dihydrogen iodide there should be repulsion between the two positively charged nitrogen atoms.



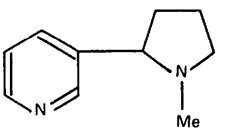
Nicotine monomethyliodide (I)



Nicotine monohydrogen iodide (II)



Nicotine dihydrogen iodide



Nicotine

Experimental. Suitable crystals for diffraction studies grown from ethanol giving transparent needles, m.p. 409·1–410·0 K (I), and large transparent lozenges, m.p. 349·3–350·9 K (II). Intensity data recorded using experimental parameters in Table 1 on Nicolet *P3m* four-circle diffractometer from crystals sealed in Lindemann-glass capillaries under dry nitrogen gas. Structures solved by Patterson and Fourier techniques using unique absorption-corrected intensities. All non-hydrogen atoms refined with anisotropic thermal parameters; hydrogen atoms in (I) constrained geometrically to ride on ligated atom, those in (II) independently located and refined with unconstrained isotropic thermal parameters.‡

‡ Lists of structure factors, anisotropic thermal parameters, H-atom parameters and all bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42799 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Additional crystal and experimental data for* (I) *and* (II)

	(I)	(II)
Temperature of data collection	293 K	200 K
Independent data	2370	1901
Data used in refinement	2310	1818
$I \geq n\,\sigma(I)$: n	2	3
$R(wR)$	0·022(0·026)	0·018(0·019)
Function minimized	$\sum w(F_o - \lvert F_c \rvert)^2$	$\sum w(F_o - \lvert F_c \rvert)^2$
Weighting scheme		
$w = [\sigma^2(F) + g\,(F^2)]^{-1}$: g	0·00016	0·0001
Scan type	ω:2θ	ω:2θ
Scan range: min., max. 2θ(°)	2·9, 50	2·9, 60
Refinement type	Block-cascade least squares	
Program system	*SHELXTL* (Sheldrick, 1981)	
Scattering factors and corrections for anomalous dispersion	*International Tables for X-ray Crystallography* (1974)	
Crystal size (mm)	0·3 × 0·4 × 0·5	0·2 × 0·25 × 0·35
Absorption correction		
empirical (μr)	0·75	0·4
max., min. transmission coefficients	0·192, 0·147	0·363, 0·335
Range of $h\,k\,l$	$\bar{1}7$,0,0–17,10,13	0,0,0–20,15,12
Intensity variation of standards (%)	1·3	1·7
Frequency of standards	100	50
Unit-cell-determining reflections; 2θ range	15; 19≤2θ≤36°	15; 27≤2θ≤30°
$\Delta\rho$, final difference Fourier map (e Å^{-3})	±0·4	±0·5
Δ/σ (final)	0·040	0·001

Table 2. *Atomic coordinates* ($\times 10^4$) *and isotropic thermal parameters* (Å$^2 \times 10^3$) *for nicotine monomethyl iodide* (I) *and nicotine monohydrogen iodide* (II)

	x	y	z	U_{eq}*
(I)				
I(1)	6400 (1)	7500	8362 (1)	65 (1)
I(2)	7682 (1)	3985 (1)	4731 (1)	76 (1)
N(1)	2916 (3)	6333 (7)	8722 (5)	80 (2)
C(2)	3628 (4)	5653 (7)	8160 (5)	64 (2)
C(3)	3520 (3)	4216 (6)	7495 (3)	46 (1)
C(4)	2619 (3)	3523 (6)	7373 (4)	52 (1)
C(5)	1886 (3)	4217 (8)	7913 (4)	63 (2)
C(6)	2068 (4)	5619 (8)	8562 (5)	70 (2)
C(7)	4342 (3)	3583 (5)	6887 (3)	44 (1)
C(8)	4115 (3)	2856 (6)	5589 (4)	54 (1)
C(9)	4955 (4)	1698 (9)	5431 (5)	72 (2)
C(10)	5597 (3)	1726 (8)	6681 (4)	63 (2)
N(11)	4938 (2)	2264 (5)	7624 (3)	48 (1)
C(12)	5497 (4)	2872 (8)	8785 (4)	69 (2)
C(13)	4311 (3)	907 (6)	7957 (5)	58 (1)
N(1′)	384 (3)	9253 (7)	11003 (4)	66 (1)
C(2′)	−185 (3)	8889 (7)	9941 (4)	54 (1)
C(3′)	104 (3)	8981 (6)	8756 (4)	46 (1)
C(4′)	1059 (3)	9428 (7)	8667 (7)	56 (1)
C(5′)	1627 (3)	9825 (7)	9744 (5)	62 (2)
C(6′)	1277 (4)	9739 (7)	10871 (5)	66 (2)
C(7′)	−628 (3)	8573 (5)	7642 (4)	47 (1)
C(8′)	−288 (3)	7613 (7)	6580 (4)	58 (1)
C(9′)	−955 (4)	8147 (8)	5401 (5)	68 (2)
C(10′)	−1645 (3)	9312 (7)	5863 (4)	63 (2)
N(11′)	−1083 (2)	10055 (5)	7000 (3)	45 (1)
C(12′)	−1736 (3)	10922 (7)	7801 (5)	56 (1)
C(13′)	−357 (3)	11220 (7)	6618 (4)	55 (1)
(II)				
I	1155 (1)	1565 (1)	421 (1)	29 (1)
N(1)	3907 (2)	−5391 (3)	12153 (3)	33 (1)
C(2)	4191 (2)	−4122 (3)	11922 (4)	30 (1)
C(3)	3922 (2)	−3352 (3)	10613 (3)	25 (1)
C(4)	3337 (2)	−3937 (3)	9462 (4)	30 (1)
C(5)	3050 (2)	−5263 (3)	9662 (4)	33 (1)
C(6)	3345 (2)	−5937 (3)	11027 (4)	32 (1)
C(7)	4261 (2)	−1910 (3)	10549 (4)	27 (1)
C(8)	3467 (3)	−843 (3)	10370 (5)	38 (1)
C(9)	3985 (2)	375 (3)	9634 (5)	39 (1)
C(10)	4981 (2)	−125 (3)	9074 (3)	31 (1)
N(11)	4905 (2)	−1631 (2)	9126 (3)	25 (1)
C(12)	5864 (2)	−2333 (3)	9171 (4)	36 (1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Discussion. Atomic coordinates are given in Table 2, bond lengths and interbond angles and torsion angles in Table 3. Figs. 1 and 2 show the molecular geometries and crystallographic numbering scheme for (I) and (II), respectively. Only one of the two crystallographically independent, and essentially identical, molecules is shown (Fig. 1) and discussed for (I).

Table 3. *Bond lengths* (Å) *and angles* (°) *and torsion angles* (°)

The values for molecule (2) of (I) are essentially identical.

	(I)	(II)	Nicotine dihydrogen iodide*
N(1)–C(2)	1·348 (7)	1·339 (4)	1·355
C(2)–C(3)	1·400 (7)	1·395 (4)	1·368
C(3)–C(4)	1·378 (6)	1·388 (4)	1·408
C(4)–C(5)	1·365 (7)	1·391 (4)	1·397
C(5)–C(6)	1·375 (9)	1·393 (5)	1·399
C(6)–N(1)	1·322 (7)	1·338 (4)	1·344
C(3)–C(7)	1·484 (6)	1·512 (4)	1·523
C(7)–C(8)	1·521 (6)	1·531 (4)	1·541
C(8)–C(9)	1·547 (8)	1·538 (5)	1·552
C(9)–C(10)	1·526 (6)	1·529 (5)	1·579
C(10)–N(11)	1·513 (6)	1·507 (3)	1·480
N(11)–C(7)	1·546 (5)	1·516 (4)	1·490
N(11)–C(12)	1·484 (6)	1·489 (4)	—
N(11)–C(13)	1·505 (6)	—	—
Intramolecular N(1)···N(11) distance	4·67 (1)	4·740 (5)	4·96
N(1)–C(2)–C(3)	123·4 (5)	124·0 (3)	125·5
C(2)–C(3)–C(4)	117·1 (4)	118·3 (2)	112·0
C(3)–C(4)–C(5)	120·1 (5)	118·6 (3)	122·0
C(4)–C(5)–C(6)	118·4 (5)	118·5 (3)	122·2
C(5)–C(6)–N(1)	124·4 (5)	123·8 (3)	114·3
C(6)–N(1)–C(2)	116·5 (5)	116·7 (3)	122·9
C(2)–C(3)–C(7)	119·3 (4)	118·1 (2)	123·8
C(4)–C(3)–C(7)	123·5 (4)	123·6 (2)	122·3
C(3)–C(7)–C(8)	117·2 (3)	116·5 (2)	107·2
C(3)–C(7)–N(11)	115·4 (3)	112·5 (2)	133·3
C(7)–C(8)–C(9)	105·8 (3)	105·1 (3)	102·8
C(8)–C(9)–C(10)	105·7 (4)	106·2 (2)	112·9
C(9)–C(10)–N(11)	104·6 (4)	104·8 (2)	98·8
C(10)–N(11)–C(7)	101·8 (3)	104·3 (2)	115·5
N(11)–C(7)–C(8)	103·0 (3)	102·0 (2)	106·8
C(10)–N(11)–C(12)	111·2 (3)	114·1 (2)	131·1
C(7)–N(11)–C(12)	112·6 (4)	114·0 (2)	106·2
C(10)–N(11)–C(13)	110·4 (4)		
C(7)–N(11)–C(13)	111·7 (3)		
C(12)–N(11)–C(13)	109·0 (4)		
Pyridine ring			
N(1)–C(2)–C(3)–C(4)	3·1 (7)	−1·1 (4)	10·8
C(2)–C(3)–C(4)–C(5)	−1·5 (7)	−0·3 (4)	−6·2
C(3)–C(4)–C(5)–C(6)	0·7 (7)	1·3 (4)	3·0
C(4)–C(5)–C(6)–N(1)	−1·4 (9)	−1·2 (5)	3·2
C(5)–C(6)–N(1)–C(2)	2·8 (9)	−0·1 (5)	−7·4
C(6)–N(1)–C(2)–C(3)	−3·7 (8)	1·3 (5)	−12·3
Pyrrolidine ring			
C(7)–C(8)–C(9)–C(10)	3·6 (6)	12·5 (4)	−5·1
C(8)–C(9)–C(10)–N(11)	23·3 (6)	13·6 (3)	13·7
C(9)–C(10)–N(11)–C(7)	−40·8 (5)	−35·0 (3)	−18·3
C(10)–N(11)–C(7)–C(8)	42·8 (4)	42·5 (3)	−16·7
N(11)–C(7)–C(8)–C(9)	−28·5 (5)	−33·5 (3)	6·0
Link between rings			
N(1)–C(2)–C(3)–C(7)	178·7 (4)	177·2 (3)	−175·4
C(2)–C(3)–C(7)–C(8)	−139·3 (4)	−123·8 (3)	−122·0
C(2)–C(3)–C(7)–N(11)	99·1 (5)	118·9 (3)	103·3
C(2)–C(3)–C(7)–H(7)†	−21	3 (2)	
C(4)–C(3)–C(7)–H(7)†	155	179 (2)	
C(5)–C(4)–C(3)–C(7)	−176·9 (4)	−178·5 (3)	171·0
C(4)–C(3)–C(7)–C(8)	36·1 (6)	54·4 (4)	75·0
C(4)–C(3)–C(7)–N(11)	−85·6 (5)	−62·8 (3)	−59·9

* Koo & Kim (1965).

† H(7) position was fixed in (I), refined in (II).

The intramolecular separation of the two nitrogen atoms, N(1) and N(11), is significantly greater in the dihydrogen than in the monohydrogen or monomethyl iodide molecules (Table 3); in all three compounds the nitrogen atoms are orientated away from each other. In the dihydrogen iodide electrostatic repulsion between the positive charges on the two nitrogen atoms might be expected to produce the greatest possible separation, yet the arrangement of C(2) and N(11) about the C(3)–C(7) bond is not fully *transoid*. Fig. 3(*a*) shows the superposition of the dihydrogen iodide (non-hydrogen atoms) and the monohydrogen iodide. The C(2)–C(3)–C(7)–N(11) torsion angle about the bond linking the rings is less in the dihydrogen (103·3°) than in the monohydrogen iodide (118·9°) but the C(3)–C(7)–N(11) angle is much greater for the former (133 compared with 113°). This could explain the greater N···N separation in the dihydrogen iodide, since the pyrrolidine ring is bent away from the pyridine ring rather than the molecule being twisted about the C(3)–C(7) bond [Fig. 3(*a*)].

The torsion angles (Table 3) indicate that the pyridine rings are essentially planar, whereas the pyrrolidine rings in (I) and (II) are appreciably folded. Fig. 3(*b*) shows the superposition of the pyrrolidine rings in (I) and (II). The difference between the C(2)–C(3)–C(7)–N(11) torsion angles in (I) and (II) is significant (119 compared with 99°), although the C(3)–C(7)–N(11) angle is similar for the two molecules (115 and 113°, respectively). These variations are consistent with the belief that steric constraints cause the additional methyl group on N(11) in (I) to adopt an axial configuration. The short intramolecular contacts in the monomethyl iodide (Fig. 1) between H(4) and the C(13) methyl hydrogens (≥2·53 Å) support the idea of there being restricted rotation about the C(3)–C(7) bond. There are no intermolecular contacts <2·8 Å in (I) or (II).

The biological reason why nicotine monohydrogen iodide is more suitable than the dihydrogen iodide for comparison with other nicotine-like compounds has been given above. The results herein provide additional support, since they indicate that there are appreciable structural differences between the two and also give substance to the previous speculation about the preferred conformation of nicotine based on NMR studies (Chynoweth, Ternai, Simeral & Maciel, 1973). In the monohydrogen iodide the separations of the charged pyrrolidine nitrogen atom, N(11), and (*a*) the pyridine nitrogen atom, N(1), (*b*) C(2) and (*c*) C(4) are 4·740 (5), 3·560 (5) and 3·160 (5) Å, respectively. In acetylcholine the separation between the quaternary nitrogen atom and (*a*) the carbonyl oxygen, (*b*) the carbonyl carbon atom, and (*c*) the ether oxygen atom, are 4·5–5·0, 4·0–4·4 and 3·0–3·3 Å, estimated from the results of Svinning & Sørum (1975) for acetylcholine bromide and the three tartrate salts studied by Jensen (1982). In nicotine, C(2) and C(4) of the pyridine ring, by analogy with pyridine itself (Longuet-Higgins & Coulson, 1947), should carry a partial positive charge and it therefore seems plausible to suppose that C(4) and N(11) in nicotine and nicotine

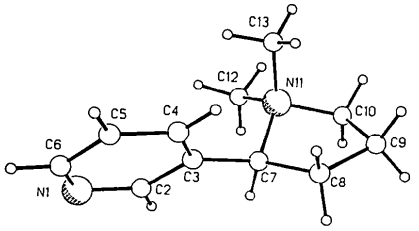

Fig. 1. Molecular structure of one crystallographically independent molecule of nicotine monomethyl iodide (I), giving the atomic numbering scheme.

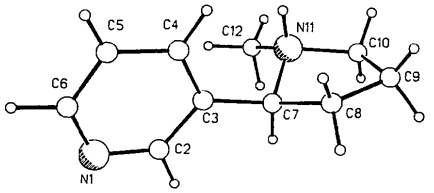

Fig. 2. Molecular structure of nicotine monohydrogen iodide (II) and the atomic numbering scheme.

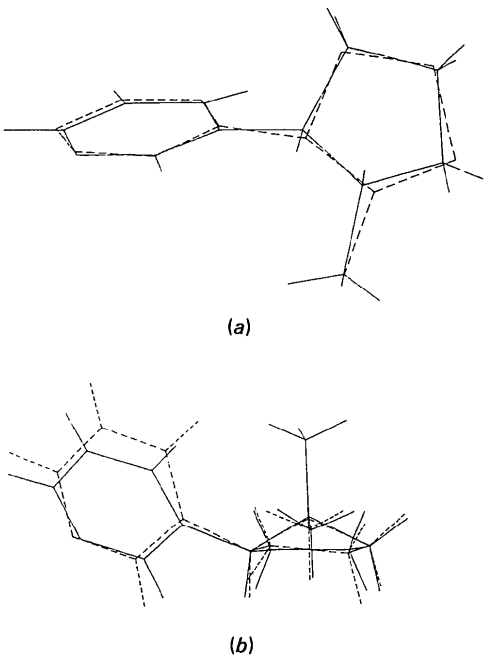

Fig. 3. Crystallographic fitting of (*a*) nicotine monohydrogen iodide (solid) and nicotine dihydrogen iodide (dashed), (*b*) the pyrrolidine rings of nicotine monomethyl (solid) and monohydrogen iodides (dashed).

monomethyl iodide are in similar environments to the ether oxygen and quaternary ammonium nitrogen atoms in acetylcholine. It has been suggested (Hey, 1952; Albert, 1979) that these may be 'pharmacodynamic' groups associated with nicotine-like activity, although the stereospecificity of nicotine indicates that there are more than two groups involved in producing the response.

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The Structures of Two Chiral Bicyclic Phosphonamides

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Abstract. The crystal structures of two enantiomerically related phosphonamides have been determined by X-ray diffraction. Cu $K\bar{\alpha}$, $\lambda = 1{\cdot}54178$ Å, room temperature. Compound (3), 2-*sec*-butyl-2,3,3a,4,5,6,7,7a-octahydro-1,3-dimethyl-1*H*-1,3,2-benzodiazaphosphole 2-oxide, $C_{12}H_{25}N_2OP$, m.p. = 369 K, $M_r = 244{\cdot}32$, orthorhombic, $P2_12_12_1$, $a = 8{\cdot}210$ (5), $b = 9{\cdot}310$ (3), $c = 18{\cdot}384$ (10) Å, $V = 1405$ Å^3, $Z = 4$, $D_m = 1{\cdot}14$, $D_x = 1{\cdot}155$ Mg m^{-3}, $\mu = 1{\cdot}60$ mm^{-1}, $F(000) = 536$. Compound (4), 2,3,3a,4,5,6,7,7a-octahydro-1,3-dimethyl-2-(1-methyl-3-butenyl)-1*H*-1,3,2-benzodiazaphosphole 2-oxide, $C_{13}H_{25}N_2OP$, m.p. = 360–362 K, $M_r = 256{\cdot}33$ orthorhombic, $P2_12_12_1$, $a = 8{\cdot}292$ (3), $b = 10{\cdot}047$ (1), $c = 17{\cdot}876$ (2) Å, $V = 1489$ Å^3, $Z = 4$, $D_m = 1{\cdot}13$, $D_x = 1{\cdot}143$ Mg m^{-3}, $\mu = 1{\cdot}53$ mm^{-1}, $F(000) = 560$. $R = 0{\cdot}042$ with 1239 observed reflections for (3) and $R = 0{\cdot}039$ with 1621 observed reflections for (4). Except for a difference in the substituents attached to P, the two molecules are mirror images of one another, thus clearly confirming the chirality-controlling reactions. Each molecule is constituted of a five-membered ring of the envelope type including a tetrahedrally coordinated phosphorus atom. To this five-membered ring is fused a cyclohexane ring in the chair conformation.

Introduction. In previous work from these laboratories we reported on the design, synthesis and reactivity of the enantiomeric chiral and topologically unique bicyclic phosphonamides (1) and (2) (Hanessian, Delorme, Beaudoin & Leblanc, 1984, 1985). Inherent in the design of these compounds were elements of chirality, stereoelectronic effects and symmetry, associated with the general structure in question. Based on these features, it was anticipated that the anion generated from the (*R*,*R*) isomer, for example, would have a *pro-S* bias in reactions with carbonyl compounds and electrophiles. Indeed, when the potassium salt was allowed to react with 4-butylcyclohexanone, the corresponding ethylidene derivative was obtained with better than 90% enantiomeric excess (Hanessian *et al.*, 1984, 1985). In order to assess the facial selectivity of the corresponding phosphonamide anion, reaction was affected with various alkyl halides. In this instance, the orientation of the newly introduced alkyl group would reflect the diastereofacial bias of the phosphonamide anion.

Thus, when the lithium or potassium anions of (1) and (2) were treated respectively with ethyl iodide and allyl bromide, crystalline products (3) and (4) were formed in high yield in each case. X-ray crystal-

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