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The Crystal Structure and Molecular Conformation of *trans*-2,5-Dimethylpiperazine Dihydrochloride

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The molecular conformation and crystal structure of *trans*-2,5-dimethylpiperazine dihydrochloride, $C_6H_{14}N_2.2HCl$, have been determined from X-ray diffractometer data. The crystals are monoclinic, space group $P2_1/n$, with unit-cell dimensions: $a = 11{\cdot}157$ (6), $b = 6{\cdot}823$ (5), $c = 6{\cdot}341$ (5) Å, $\beta = 102{\cdot}16$ (10)°; $Z = 2$. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to $R = 0{\cdot}057$ for 543 independent reflections. The *trans*-2,5-dimethylpiperazine ring adopts an almost ideally puckered chair conformation with the side methyl groups in the equatorial position. The endocyclic bond data are: ⟨C—N⟩, 1·503 (9) Å; C—C, 1·534 (12) Å; ⟨C—C—N⟩, 108·7 (3)°; ⟨C—N—C⟩, 112·4 (3)°; average torsion angle, 58·9°. The crystal structure consists of strongly hydrogen-bonded molecules (N—H···Cl, 3·07–3·08 Å; H···Cl, 2·00–2·01 Å; ∠N—H—Cl, 170–172°) residing at crystallographically imposed centres of symmetry.

Introduction

In the course of structural studies of crystalline polymers obtained by interfacial and solution polycondensation of fumaroyl dichloride with *trans*-2,5-dimethylpiperazine, to form poly(*trans*-2,5-dimethyl-1,4-piperazinedifumaroyl) (Mortillaro, Russo, Guidotti & Credali, 1970) several model compounds were examined by X-ray diffraction. In a previous paper (Bassi & Scordamaglia, 1977) we reported the molecular structure of 1,4-bis(chloroacetyl)-*trans*-2,5-dimethylpiperazine. We now extend this work to *trans*-2,5-dimethylpiperazine dihydrochloride, $H_2P^{2+}.2Cl^-$.

The molecular structure of $H_2P^{2+}.2Cl^-$ presents various interesting features as the introduction of a hetero-atom into a six-membered homocyclic system brings about many changes in overall symmetry, molecular shape and chemical and physical properties. Conformational studies on such heterocycles, *e.g.* piperidine, piperazine and morpholine in solution by means of spectroscopic methods and dipole moment measurements have previously been concerned in particular with the problem of the equatorial/axial position of the nitrogen-bound substituent group, either in the presence or absence of environmental influences, as well as with the steric requirements of the nitrogen lone-pair electrons (Aroney & Le Fèvre, 1958; Aroney, Chen, Le Fèvre & Saxby, 1964; Bishop, Sutton, Dineen, Jones & Katritzky, 1964; Allinger, Carpenter & Karkowski, 1965; Lambert & Keske, 1966; Allinger, Hirsch & Miller, 1967; Lambert, Bailey & Michel, 1970). Of course, these methods do not yield as much detailed quantitative information as diffraction methods, but, in general, the results support the chair shape for these molecules with equatorial substituents (Allinger, Carpenter & Karkowski, 1965; Lambert & Keske, 1966; Riddell, 1967; Bastiansen, Seip & Boggs, 1972). Nevertheless, conflicting conformational assignments have been reported. It has been stated (George & Wright, 1958; Aroney & Le Fèvre, 1960) that piperazine and some of its 1,4-disubstituted derivatives occur partly in a boat form with the N—H and N—Me bonds being sometimes equatorial and sometimes axial and the N—Ar bonds always equatorial. Contrary to this, consideration of torsional barriers predicts the absence of any significant amount of the non-chair form in simple piperazine derivatives (Wilson, 1959).

Because there are several reasonable assumptions involved in the previous work, it is useful to establish the exact geometry of some of these compounds by means of X-ray diffraction techniques. This allows in particular a more detailed examination of the substituent effect upon ring flattening. As to the latter, we notice that the calculation of dipole moments, molar Kerr constants and other properties has often been based on approximate geometrical parameters only (*cf.* Aroney & Le Fèvre, 1958; Aroney, Chen, Le Fèvre & Saxby, 1964; Allinger, Hirsch & Miller, 1967, and others) and is therefore open to criticism as the effect of ring flattening has not properly been accounted for. Consequently, conclusions with regard to the distribution of chair and boat forms in solution might be affected.

Experimental

After initial examination on a Weissenberg camera, a transparent crystal of $C_6H_{14}N_2.2HCl$ of parallelepipedal shape and approximate dimensions 0·3 × 0·3

× 0·5 mm was mounted on a Picker FACS 1 four-circle computer-controlled diffractometer equipped with a scintillation counter and a pulse-height analyser.

The orientation matrix and unit-cell dimensions with their e.s.d. values were obtained from a least-squares fit of χ, φ, ω and 2θ values from 12 independent reflections. Intensity data were collected with zirconium-filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å) in the angular range $5° \le 2\theta \le 60°$, using the moving-crystal moving-counter technique with a 2θ scan rate of 1° min^{-1} and a scan range of ($2{\cdot}0° + \Delta$), where Δ was varied to allow for the separation of the $K\alpha_1$ and $K\alpha_2$ peaks at increasing 2θ values. Background counts were measured for 10 s each at the extremes of each scan. Three standard symmetry-equivalent reflections were measured periodically to monitor intensity fluctuations during the data collection (±2%). Of the 763 independent reflections measured, 543 were assumed to be significant according to the criterion $I \ge 3\sigma(I)$ $\{\sigma = [N_s + (t_s/t_b)^2 N_b]^{1/2}$, where N_s is the total peak count during the time of scanning t_s, and t_b is the time spent in measuring the N_b background counts$\}$. An arbitrary intensity equal to 0·5 times the observable limit was assigned to the non-significant reflections. All intensities were corrected for Lorentz and polarization effects, but not for absorption ($\mu = 6{\cdot}20$ cm^{-1}).

Crystal data

$C_6H_{14}N_2.2HCl$, $M_r = 187{\cdot}12$, monoclinic, $a = 11{\cdot}157\,(6)$, $b = 6{\cdot}823\,(5)$, $c = 6{\cdot}341\,(5)$ Å, $\beta = 102{\cdot}16\,(10)°$; $U = 471{\cdot}87$ Å^3, $D_m = 1{\cdot}33$, $D_c = 1{\cdot}32$ g cm^{-3}, $Z = 2$, $F(000) = 200$. Space group $P2_1/n$ from systematic absences $0k0$ for k odd and $h0l$ for $h + l$ odd.

Structure determination

The structure was solved by the heavy-atom method (three-dimensional Patterson map). A Fourier map phased on the chlorine atoms permitted location of all non-hydrogen atoms of the molecule. Refinement was performed by means of a general least-squares program (Immirzi, 1967), which minimizes $[\sum w(|F_o| - |F_c|)^2]$. Atomic scattering factors were calculated according to Vand, Eiland & Pepinsky (1957) with the values of Moore (1963) for the parameters. Weights were attributed according to Cruickshank, Pilling, Bujosa, Lovell & Truter (1961). After full-matrix least-squares refinement of the positional and isotropic thermal parameters the conventional $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ value was 0·12 for the 543 significant reflections; allowance for thermal anisotropy reduced R to 0·067. Hydrogen atoms were then introduced into the structure factor calculations according to the indications from a difference map and on stereochemical grounds (C—H and N—H = 1·08 Å). In the last refinement stage, only the parameters of the non-hydrogen atoms were allowed to vary until the shifts were negligibly small and well below the corresponding e.s.d. The final R value was 0·057 for the non-zero reflections.*

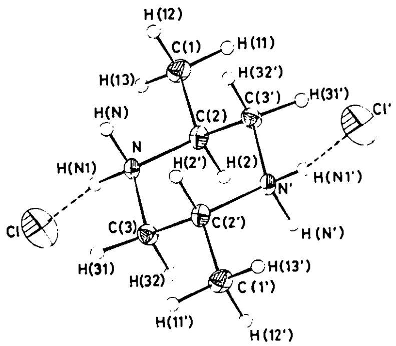

Fig. 1. Projection along the *c* axis of the *trans*-2,5-dimethylpiperazine dihydrochloride molecule, indicating the atom labelling scheme, and the 30% probability thermal vibration ellipsoids.

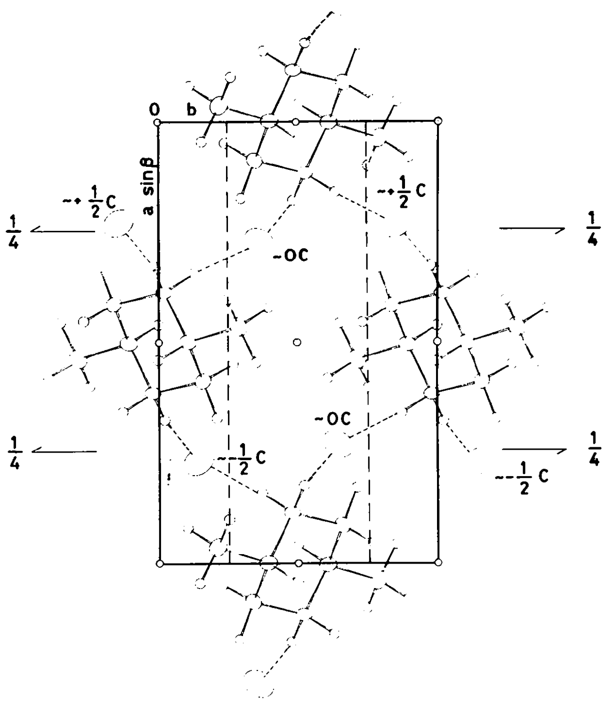

Fig. 2. Packing arrangement in *trans*-2,5-dimethylpiperazine dihydrochloride as viewed down the *c* axis.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33504 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Final fractional coordinates of the atoms of* $C_6H_{14}N_2.2HCl$ *in the asymmetric unit*

The estimated standard deviations are given in parentheses as variations of the last significant digit. B for the H atoms = 5·0 Å^2.

	x	y	z
Cl	0·22957 (13)	0·85632 (25)	0·43162 (23)
N	0·3852 (4)	1·0201 (8)	0·8529 (8)
C(1)	0·4634 (6)	1·2871 (11)	0·6581 (11)
C(2)	0·4983 (5)	1·1066 (10)	0·7966 (10)
C(3)	0·4126 (6)	0·8400 (9)	0·9921 (10)
H(11)	0·545	1·350	0·621
H(12)	0·420	1·394	0·745
H(13)	0·401	1·246	0·512
H(2)	0·540	1·000	0·709
H(N)	0·342	1·128	0·936
H(N1)	0·323	0·977	0·704
H(31)	0·328	0·790	1·030
H(32)	0·452	0·732	0·907

Table 2. *Bond data of trans-2,5-dimethylpiperazine dihydrochloride*

(*a*) Bond lengths (Å)

N–C(2)	1·503 (8)
N–C(3)	1·504 (10)
C(1)–C(2)	1·514 (12)
C(2)–C(3)	1·534 (12)

(*b*) Bond angles (°)

N–C(2)–C(3′)	107·9 (3)
N–C(2)–C(1)	109·5 (3)
N–C(3)–C(2′)	109·4 (2)
C(1)–C(2)–C(3′)	110·7 (3)
C(2)–N–C(3)	112·4 (3)

(*c*) Torsion angles (°)

C(2)–N–C(3)–C(2′)	60·1
N–C(3)–C(2′)–N′	−57·4
C(3)–N–C(2)–C(3′)	−59·3
Average	58·9
N–C(3)–C(2′)–C(1′)	183·1
C(1′)–C(2′)–N′–C(3′)	179·7

(*d*) Non-bonded distances (Å)

Cl···N	3·073 (5)	N···N′	2·851 (11)
Cl′···N	3·083 (5)	C(2)···C(2′)	2·954 (15)
Cl···H(N′)	2·00	C(3)···C(3′)	2·915 (15)
Cl′···H(N)	2·01	C(1)···C(3′)	2·508 (8)
		C(1)···N	2·462 (9)

Results and discussion

The molecular conformation and crystal structure of *trans*-2,5-dimethylpiperazine dihydrochloride as obtained from the final parameters in Table 1 are shown in *c*-axis projection in Figs. 1 and 2. The geometrical parameters of the molecule with their e.s.d.'s are listed in Table 2. The ring adopts an almost ideally puckered chair conformation with the methyl groups in the 2 and 5 positions in the diequatorial conformation. We notice that the H_2P^{2+} ring exhibits space-group imposed $\bar{1}$ (C_i) symmetry, which obviously immediately rules out the chair conformation *ae* as well as any boat form in an ordered crystal structure. The endocyclic bond lengths are: C–N$^+$ = 1·503 (9) (average), C–C = 1·534 (12) Å. The former is slightly longer than usually found for C–N$^+$ single bonds, namely about 1·47–1·49 Å in dimethylammonium and dicyclohexylammonium cations (Caputo & Willett, 1976; Wood, Sax & Pletcher, 1975; Rao & Sundaralingam, 1969). The C–C bond length closely conforms to that reported recently in structural studies of vapour-phase *n*-alkanes (1·531 Å) (Bradford, Fitzwater & Bartell, 1977) and in cyclohexane (1·520 Å) (Buys & Geise, 1970).

The endocyclic C–C–N bond angles average to 108·7 (3) and the C–N–C angle to 112·4 (3)°. Clearly, the force constants for bond-angle deformation at the hetero-atom differ from that of carbon. The average endocyclic bond angle in $H_2P^{2+}.2Cl^-$ (109·9°) departs slightly from the value of 111·05° for the bond angle in the chair conformation of cyclohexane, according to electron diffraction analysis (Buys & Geise, 1970) and the calculated minimum energy conformation (Bucourt & Hainaut, 1965; Bixon & Lifson, 1967). Similar values (111·0–111·5°) were observed in cyclohexylammonium salts (Rao & Sundaralingam, 1969; Wood, Sax & Pletcher, 1975). The average value of the ring torsional angles found is $58{\cdot}9_3$° (maximum 60·1°, minimum 57·4°). The torsional interactions along the hetero-atom–carbon bonds differ from those along carbon–carbon bonds and are in accordance with the fact that six-membered-ring molecules with heavy atoms are more puckered (Romers, Altona, Buys & Havinga, 1969) than cyclohexane (55·9°) (Buys & Geise, 1970). Owing to the precise mathematical relations between the geometrical parameters in closed rings, it is not surprising that introduction of a nitrogen atom influences the other internal bond angles and torsional angles. If we apply the expression $\cos\langle\varphi\rangle = -\cos\langle\theta\rangle/(1+\cos\langle\theta\rangle)$, relating the torsional angle φ and the endocyclic valency angle θ of a six-membered heterocyclic ring in the chair conformation (point group D_{3d}) (Pauling, 1949; Dunitz, 1970), we obtain $\langle\varphi\rangle_{\rm calc} = 58{\cdot}9_6$° ($\langle\varphi\rangle_{\rm obs} = 58{\cdot}9_3$°) for $\langle\theta\rangle$ = 109·9°. This shows that the H_2P^{2+} ring is here only slightly flatter than the cyclohexane perfect-chair model, which implies tetrahedral bond angles and torsional angles of ±60°.

It is of interest to compare our results with those of other piperazines. In particular, the extent of ring deformation in H_2P^{2+} as compared to piperazine is most noteworthy (*cf.* Table 3), especially if we consider that substituents usually flatten rather than pucker a ring (Altona & Sundaralingam, 1970). Apparently, rehybridization of the nitrogen atoms upon protonation is considerable and introduces the additional strain in the molecule which also requires further deformation of the bond angles. The interpretation of Sudmeier (1968) of the vicinal-coupling constants in NMR data for $H_2P^{2+}.2Cl^-$ (as well as for *trans*-2,5-dimethylpiperazine and its monohydrochloride), based on a

Table 3. *Selected bond data in some substituted six-membered heterocyclic compounds*

		Endocyclic bond data[(a)]							
Compound	Conformation	C–C	C–N	C–C–N	C–N–C	$\langle\varphi_{calc}\rangle$	$\langle\varphi_{obs}\rangle$	Method[(b)]	Reference[(d)]
Piperazine	Chair	1·527 (5)	1·471 (5)	109·8 (5)	112·6 (5)	56·8	–	*E*	Davis & Hassel (1963)
N,*N*-Dimethyl-piperazine	Chair	1·521 (10)	1·457 (10)	110·3 (10)	114·4 (10)	54·1	–	*E*	Davis & Hassel (1963)
N,*N*-Dichloro-piperazine	Chair	1·54 (–)	1·47 (–)	109·5 (–)[(c)]	109·5 (–)[(c)]	60·0	–	*E*	Andersen & Hassel (1949)
Piperidine hydrochloride	Chair	1·505 (n.d.)	1·497 (n.d.)	110·4 (n.d.)	112·3 (n.d.)	54·30	54·32	*X*	Rérat (1960)
trans-2,5-Dimethyl-piperazine dihydro-chloride	Chair; *ee*	1·534 (12)	1·503 (9)	108·70 (25)	112·43 (25)	58·96	58·93	*X*	This work
1,4-Bis(chloroacetyl)-*trans*-2,5-dimethyl-piperazine	Chair; *aa*	1·520 (5)	1·471 (5)	111·57 (9)	114·61 (15)	53·60	53·65	*X*	Bassi & Scordamaglia (1977)
1-Piperidino-1-benzylcyclohexane	Chair; *e*	1·505 (10) 1·504 (10)	1·462 (8) 1·465 (7)	110·0 (6) 110·3 (5)	109·7 (4) 109·4 (4)	57·61 57·61	57·47[(e)] 57·44[(e)]	*X*	Ducruix & Pascard-Billy (1974)

Notes: (*a*) Bond lengths (Å), bond angles and torsion angles (°). (*b*) *X*, X-ray diffraction; *E*, electron diffraction. (*c*) Assumed values. (*d*) Mann & Senior (1953) describe the chair conformation of 1,2,2,4,5,5-hexamethylpiperazine dinitrate as *aaeaae* or *eaeeae*. (*e*) Range from 52·5° to 62°.

supposed decrease in the endocyclic N—C—C angles due to nitrogen rehybridization with protonation (and consequent increase in the geminal H—C—H angle) thus fits the experimental data. Our findings of the equatorial positions of the side groups in $H_2P^{2+}.2Cl^-$ also agree with those of Sudmeier (1968) and apply to the corresponding monohydrochloride. Similarly, *N*-methylpiperidine shows energetic preference for a methyl group in the equatorial position (Allinger, Carpenter & Karkowski, 1965). In contrast, in 1,4-bis-(chloroacetyl)-*trans*-2,5-dimethylpiperazine (I) the side methyl groups take up axial positions to avoid too short contact distances between the methyl groups and an oxygen and carbon atom (Bassi & Scordamaglia, 1977). This results in a more pronounced flattening of the *trans*-2,5-dimethylpiperazine ring in (I) than in $H_2P^{2+}.2Cl^-$, exceeding also that of the unsubstituted piperazine ring. An analogous situation is reported (Romers, Altona, Buys & Havinga, 1969) for 1,4-dioxane ($\langle\varphi\rangle = 57{\cdot}9°$) and for *trans*-2,5-dichloro-1,4-dioxane with its axial substituents ($\langle\varphi\rangle = 51{\cdot}9°$). Where the substituents are in equatorial positions the flattening of the ring seems to be less pronounced.

With regard to the non-bonded interactions in $H_2P^{2+}.2Cl^-$, the axial H—H interactions across the ring are in the range 2·50–2·54 Å, well above twice the van der Waals radius of hydrogen. The shortest intermolecular distances are reported in Table 4. The packing of $H_2P^{2+}.2Cl^-$ is dictated by the requirements of the crystallographically imposed symmetry sites, hydrogen-bond formation and the size of the large chloride ions. Each chloride ion is fixed to one of the hydrogens residing at a nitrogen atom with the other quaternary ammonium hydrogen atom forming a bridge to a chlorine atom of a neighbouring $H_2P^{2+}.2Cl^-$ molecule. Such an involvement of both hydrogen atoms of the $>\overset{+}{N}H_2$ group to form N—H···Cl bonds is usual in chloride salts of organic bases (Donohue, 1952). The arrangement leads to a tight two-dimensional network, well in accordance with the low temperature factors observed. Apparently, it is

Table 4. *Short intermolecular distances* (Å)

The symbols *A* and *B* denote molecules at *x*,*y*,*z* and $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$ respectively. In this notation A_{000} stands for the reference molecule and $B_{\alpha\beta\gamma}$ indicates fractional coordinates $\alpha+\frac{1}{2}+x$, $\beta+\frac{1}{2}-y$, $\gamma+\frac{1}{2}+z$. The primed atoms are related to the atoms of the asymmetric unit by the requirements of the crystallographically imposed centre of symmetry. Intermolecular distances are arbitrarily limited at the sum of the van der Waals radii plus 0·4 Å.

A_{000}	$B_{\bar{1}\bar{1}\bar{2}}$		A_{000}	$A_{0\bar{1}1}$	
Cl	C(1′)	3·93	C(1′)	H(11)	3·03
Cl	H(13′)	2·98			
A_{000}	$B_{\bar{1}\bar{1}\bar{1}}$		A_{000}	$A_{00\bar{1}}$	
Cl	N′	3·08	Cl	C(1′)	3·72
Cl	C(1′)	3·74	Cl	C(2′)	3·64
Cl	C(2′)	3·77	Cl	C(3)	3·79
Cl	C(3)	3·87	Cl	H(11′)	2·96
Cl	C(3′)	3·94	Cl	H(21)	3·05
Cl	H(12′)	2·92	Cl	H(31)	3·01
Cl	H(2)	3·33	C(1)	H(21)	3·04
Cl	H(N′)	2·01	C(2)	H(21)	3·23
Cl	H(32)	3·13	H(13)	H(21)	2·37
			H(2)	H(21)	2·62
A_{000}	$B_{\bar{1}0\bar{1}}$		A_{000}	$A_{01\bar{1}}$	
Cl	C(1)	3·95	C(1)	C(1′)	3·72
Cl	C(3′)	3·74	C(1)	H(11′)	3·03
Cl	H(11)	3·23	H(11)	H(11′)	2·62
Cl	H(31′)	3·05			
C(1)	H(31′)	3·22			
H(13)	H(31′)	2·53			
A_{000}	$A_{0\bar{1}0}$		A_{000}	$B_{0\bar{1}0}$	
H(12′)	H(32′)	2·52	Cl′	C(1′)	3·95
			Cl′	C(3)	3·74
			Cl′	H(11′)	3·23
			Cl′	H(31)	3·05
			C(1′)	H(31)	3·22
			H(13′)	H(31)	2·53

sterically possible to satisfy all packing requirements simultaneously, as the N—H···Cl bonds in $H_2P^{2+}.2Cl^-$ are amongst the shortest ones observed so far, namely 3·07 and 3·08 Å, *i.e.* in the lower range of the usually reported values from 3·0 to 3·3 Å (Donohue, 1952; Rérat, 1960) and much shorter than the sum of the van der Waals radii. This is in accordance with the fact that strong hydrogen bonding occurs when the hydrogen atom is collinear with the bonded atoms. In $H_2P^{2+}.2Cl^-$ the two independent N—H···Cl angles are 170 (2) and 172 (2)°. Consequently, it is not surprising that the N···Cl and N···Cl′, N—C(2) and N—C(3) links form an almost regular tetrahedron around the nitrogen atom:

Cl—N—Cl′	116·39 (20)°	Cl′—N—C(2)	105·14 (29)°
Cl—N—C(2)	106·57 (28)	Cl′—N—C(3)	113·55 (27)
Cl—N—C(3)	102·73 (30)	C(2)—N—C(3)	112·43 (25).

The two independent Cl···H bond distances are very similar and amount to 2·00 and 2·01 Å.

It may be argued that the requirements of the crystal structure may eventually alter the molecular conformation. Nevertheless, the difference in conformation of the molecules in the similarly hydrogen-bonded crystal structure of piperidine hydrochloride, in which the average torsional angle amounts to only 54·32°, is still significant.

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