The origin of the splitting of ^{13}C and ^{15}N NMR signals of 3(5)-phenyl-5(3)-methylpyrazolium chloride and bromide in the solid state: Quantum Espresso calculations

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HIGHLIGHTS

- The ^{13}C and ^{15}N CPMAS NMR spectra of two pyrazolium salts have been recorded.
- DFT D and Quantum Espresso calculations have been performed on the chloride.
- Only Quantum Espresso calculations are able to reproduce the experimental splittings.
- There is a biunivocal relationship between X ray geometries and SSNMR chemical shifts.

GRAPHICAL ABSTRACT

The origin of the very clear splittings observed for the title compound has been ascertained through Quantum Espresso calculations.

ABSTRACT

A combination of ^{13}C and ^{15}N CPMAS NMR spectroscopy and theoretical methods (DFT and DFT D) was used to discuss the observation of large splittings affecting some atoms in 3(5) phenyl 5(3) methylpyrazolium chloride and bromide. Conventional calculations using fully optimized structures with C_2 symmetry reproduce solution spectra, but the large splitting observed for the signals of several pyrazolium carbon and nitrogen atoms in the solid state can only be explained by calculations employing the experimental $\text{P}2_1/n$ geometry and periodic boundary calculations.

Keywords:

Pyrazolium salts
SSNMR
CPMAS
DFT-D calculations
Quantum Espresso

Introduction

There are at least four main causes to explain additional splittings observed in solid state NMR (SSNMR) when compared with solution spectra [1]: (i) the existence of two or more independent molecules in the unit cell that in solution are dynamically averaged into a unique structure; (ii) crystal field effects that reduce the effective symmetry of the molecules in the solid; (iii) the presence of restricted rotations and conformations that become free in solution because of low barriers; (iv) the effect of quadrupolar nuclei like ^{14}N , $^{35(37)}\text{Cl}$ and $^{79(81)}\text{Br}$. Obviously these factors can coexist and in many cases only computational methods can be used to determine their relative importance. In previous work, we have found that the pyrazolium salts 3(5) phenyl 5(3) methylpyrazolium chloride (1) and 3(5) phenyl 5(3) methylpyrazolium bromide (2) show some signals that appear as doublets [2]. In this paper we present results of a number of different DFT and DFT D calculations performed to elucidate the origin of the observed splittings. Calculations are based on the known X ray structures of both salts (SEGNIB and SEGNOH, respectively) [3]. These structures show a dimer structure with two cations and two anions; the non hydrogen atoms of the central pseudo ring form a sort of cyclohexane, chair for the chloride 1 and boat for the bromide 2 both close to the planarity (Fig. 1 bottom). Additionally we present calculations with periodic boundary conditions of chemical shifts using optimized crystal structures, in order to explore the possibility that SSNMR could correspond to a less symmetric structure than the one observed by X ray, like it was reported by Facelli and Grant for naphthalene [4]. These calculations are limited to the chloride 1 because there are no potentials available for bromine in Quantum Espresso calculations (see *Periodic Boundary Calculations*).

It is important to be aware that the geometries of each pyrazolium salt are different. For instance in the 3(5) phenyl 5(3) methylpyrazolium chloride (SEGNIB, 1) there are some very significant differences between molecules A and B (Table 1 and Supplementary material) mainly in what concerns the atoms C4 and C12.

Experimental

Compounds 1 and 2 were prepared following the procedure described in Ref. [2]. Crystals were obtained and their identity with previous ones checked (same unit cells).

Fig. 1. Scheme of the crystal structures [2]. Distances of the anions to the mean plane of the ten atoms of both pyrazolium rings: SEGNIB (1): 0.20 and 0.05 Å (one in each side) and SEGNOH (2): 0.22 and 0.31 Å (both in the same side).

Table 1

Some relevant geometrical parameters of SEGNIB excluding H atoms (see numbering below).

Geometry	Molecule A	Molecule B	Difference
<i>Distances (Å)</i>			
C3–C4	1.395	1.389	0.006
C4–C5	1.377	1.374	0.003
C5–C12	1.482	1.494	–0.012
<i>Angles (°)</i>			
N2–C3–C4	106.22	106.84	–0.62
C3–C4–C5	107.78	107.08	0.70
C4–C5–N1	107.04	107.53	–0.49
N1–C5–C12	121.29	120.97	0.32
C4–C5–C12	131.67	131.50	0.17

NMR

^{13}C (100.73 MHz) and ^{15}N (40.60 MHz, natural abundance) CPMAS NMR spectra have been obtained on a Bruker WB 400 spectrometer at 300 K using a 4 mm DVT probehead. Samples were carefully packed in a 4 mm diameter cylindrical zirconia rotor with Kel F end caps. Operating conditions involved $2.9\ \mu\text{s}\ 90^\circ\ ^1\text{H}$ pulses and decoupling field strength of 86.2 kHz by TPPM sequence. ^{13}C spectra were originally referenced to a glycine sample and then the chemical shifts were referred to Me_4Si using the carbonyl atom $\delta(\text{glycine})$ at 176.1 ppm as a secondary Ref. [5] and ^{15}N spectra to $^{15}\text{NH}_4\text{Cl}$ and then converted to nitromethane scale using the following relationship: $\delta^{15}\text{N}(\text{nitromethane}) = \delta^{15}\text{N}(\text{ammonium chloride}) - 338.1\ \text{ppm}$ [6].

The typical acquisition parameters for ^{13}C CPMAS were: spectral width, 40 kHz; recycle delay, 5 s; acquisition time, 30 ms; contact time, 2 ms; and spin rate, 12 kHz. In order to distinguish protonated and unprotonated carbon atoms, the NQS (Non Quaternary Suppression) experiment by conventional cross polarization was recorded; before the acquisition the decoupler is switched off for a very short time of $25\ \mu\text{s}$ [7,8]. And for ^{15}N CPMAS were: spectral width, 40 kHz; recycle delay, 5 s; acquisition time, 35 ms; contact time, 6 ms; and spin rate, 6 kHz. Typical acquisition parameters for ^{15}N CPMAS were as follows: spectral width, 40 kHz; recycle delay, 90 s; contact time, 7 ms; and spin rate, 6 kHz.

Computational details

Molecular calculations

Geometries of the different structures of compound 1 were fully optimized at the B3LYP theoretical level [9,10], with the 6 311++G(d,p) basis set [11] as implemented in the Gaussian 09 program [12]. Harmonic frequency calculations [13] verified the nature of the stationary points as minima (all real frequencies).

Fig. 2. ^1H - ^{13}C and ^1H - ^{15}N CPMAS NMR spectra acquired at 9.4 T: top: 1; bottom: 2.

^{13}C and ^{15}N absolute shieldings of compounds **1a**–**1c** have been calculated using the fully optimized geometries within the GIAO approximation [14,15]. PCM calculations [16] were used as implemented in Gaussian 09.

The absolute shieldings (σ , ppm) were transformed into chemical shifts (δ , ppm) by means of the following equations:

$$\delta^{13}\text{C} = 175.7 - 0.963\sigma^{13}\text{C} \quad (1)$$

$$\delta^{15}\text{N} = 152.0 - 0.946\sigma^{15}\text{N} \quad (2)$$

These empirical equations are only valid for GIAO/B3LYP/6-311++G(d,p) calculations. We have established these equations using a large collection of data and related the calculated values for the gas phase with experimental values determined in solution and therefore they take into account the average gas phase to solution chemical shifts.

Table 2
 ^{13}C and ^{15}N chemical shifts (ppm) of compounds **1** and **2**. In solution, both compounds are identical.

Compound		Pos. 3	Pos. 4	Pos. 5
HCl/HBr (1,2)	CD ₃ OD	148.0 (C3) 11.2 (Me)	105.7 (C4)	148.8 (C5) 127.2 (Ci) 127.8 (Co) 130.5 (Cm) 132.3 (Cp)
Present work				
HCl (1)	CPMAS	144.6 (C3) 144.0 (C3) 6.3 (Me) 9.2 (Me)	100.2 (C4) 103.8 (C4)	145.7 (C5) 125.8 (Ci) 124.6 (Ci) 126.8 (Co) 129.3 (Co) 129.9 (Co) 128.4 (Cm) 131.1 (Cm) 132.1 (Cm) 132.1 (Cp)
	^{15}N	-186.2, -187.4 (N1) -178.8, -180.8 (N2)		
HBr (2)	CPMAS	145.1 (C3) 144.4 (C3) 9.4 (Me) 11.4 (Me)	101.9 (C4) 105.3 (C4)	146.2 (C5) 124.0 (Ci) 125.7 (Co) 126.2 (Co) 127.3 (Co) 128.3 (Cm) 126.2 (Cm) 132.0 (Cm) 130.5 (Cp)
	^{15}N	-188.4, -189.7 (N1) -184.6 (N2)		

Table 3
The most split signals (all values in ppm). $\Delta\delta$ is the splitting difference.

Comp.	State	Atom	Signal 1	Signal 2	Average	Difference ($\Delta\delta$)
1	CPMAS	CH ₃	6.3	9.2	7.8	2.9
		C4	100.2	103.8	102.2	3.6
		N1	-186.2	-187.4	-186.8	1.2
		N2	-178.8	-180.8	-179.8	2.0
2	CPMAS	CH ₃	9.5	11.4	10.4	1.9
		C4	101.9	105.3	103.6	3.4
		N1	-188.4	-189.7	-189.1	1.3
		N2	-184.6	-184.6	-184.6	0
1, 2	CD ₃ OD	CH ₃	-	-	11.2 [2]	-
		C4	-	-	105.7 [2]	-

Periodic boundary calculations

Quantum Espresso (QE, www.quantum-espresso.org), was employed in all calculations using periodic boundary conditions. QE was used to optimize the crystal and the isolated dimer structures, using DFT D [19–21] and the PBE [22,23] exchange correlation functional. The density functional theory (DFT) gauge including projector augmented wave (GIPAW) [24] method with pseudopotentials to approximate the core electron wave function, as implemented in the program QE, was used to predict the ^{13}C

chemical shift tensors for all carbons, and for both configurations, crystal and isolated dimer, at the same level of theory.

The details of QE calculations are the following: (i) the ultrasoft *pbe rrjkus gipaw dc* pseudopotentials for C, H and N, and *pbe n kjpaw* pseudopotential for Cl, from www.quantum-espresso.org were tested. (ii) The convergence of the scf calculations, *conv*, was varied and set in 10^{-10} . (iii) The energy cutoff for the wavefunction, *ecutwfc*, was varied and set in 65 Ry (1 Rydberg = 13.60569253 eV). (iv) The *k* points were varied between 1 and 4 in each dimension, and set in *k* = 2. All calculations were performed using version 5.0.1 of QE.

Results and discussion

In order to verify all the SSNMR results reported previously [2], in a first step we recorded again the ^{13}C CPMAS NMR spectra and measure anew the ^{15}N CPMAS NMR spectra of compounds **1** and **2** (Fig. 2). The older spectra were recorded on a Bruker AC 200 (4.7 T) and the new ones on a Bruker WB 400, 9.4 T.

It is apparent from Fig. 2 that the new experimental spectra, taken at higher field, confirm the splitting of carbon and nitrogen signals for some nuclei (Table 2). The chemical shifts corresponding to the spectra in Fig. 2, together with some of those from our previous publication (^{13}C in CD₃OD) [2], are gathered in Table 2.

We have summarized in Table 3 the most split signals in SSNMR. They correspond to CH₃ and C4 in ^{13}C and to the nitrogen atoms in ^{15}N CPMAS. Fig. 2 shows that each pair of signals in the ^{13}C NMR spectra are approximately of the same intensity. The lower signal to noise ratio of the ^{15}N NMR spectra is due to lower abundance of ^{15}N with regard to ^{13}C , this results in “doublets” of apparent different intensity.

Although the $\Delta\delta$ values of **1** and **2** are similar, the absolute values are rather different with (average **1**) = 2.71 (CH₃), 1.66 (C4), 2.26 (N1) and 4.77 ppm (N2). The ^{13}C chemical shifts in CD₃OD are closer to those of **2** than to those of **1**. We can already note that to these signals correspond some of the larger geometry differences of Table 1 (see also Supplementary material).

Theoretical calculations

a. GIAO/B3LYP/6 311++G(d,p) calculations of dimers of C₂ symmetry.

Optimizing the molecular geometry of the dimer changes its symmetry from a starting experimental P2₁/n in the crystal structure to a C₂ after optimization (Fig. 3). On the C₂ optimized geometry we carried out calculations of the absolute shieldings (σ , ppm) and transformed them into chemical shifts (δ , ppm) with Eqs. (1) and (2) for the gas phase and for DMSO and H₂O solutions (PCM) (Table 4).

The chemical shifts calculated in the gas phase as well as those calculated using the PCM method in water and DMSO are in good agreement with the experimental values both in solution and in SSNMR. The correlations between calculated and experimental values for all possible combinations of experimental and calculated ones are very similar, with the two best given by:

$$\delta_{\text{exp}}(\text{CD}_3\text{OD}) = (1.004 \pm 0.001)\delta_{\text{calc}}(\text{H}_2\text{O}), \quad n = 16, \quad R^2 = 0.99999 \quad (3)$$

$$\delta_{\text{exp}}(\text{CPMAS}) = (0.993 \pm 0.003)\delta_{\text{calc}}(\text{gas}), \quad n = 39, \quad R^2 = 0.9998 \quad (4)$$

Note that in the correlation presented in Eq. (1) we have used the average chemical shifts of the calculated *ortho* and *meta* positions of the phenyl rings.

Fig. 3. The optimized geometry of **1**, left face; right profile (a near planar boat-like structure). Distances of the anions to the mean plane of the ten atoms of both pyrazolium rings: 0.04 Å (both in the same side, C_2). The structure of **2** is very similar with distances of the anions to the mean plane of the ten atoms of both pyrazolium rings: 0.08 Å (both in the same side, C_2).

Table 4
Experimental and calculated chemical shifts of compounds **1** and **2** corresponding to GIAO/PCM/B3LYP/6-311++G(d,p) calculations.

Salt	Atom	CD ₃ OD Exp.	CPMAS Exp.	δ Gas Calc.	δ DMSO Calc.	δ H ₂ O Calc.
1	C3	148.0	144.6	145.83	148.17	148.21
1	C3		144.0	145.83	148.17	148.21
1	C4	105.7	100.2	100.98	104.57	104.64
1	C4		103.8	100.98	104.57	104.64
1	C5	148.8	145.7	146.59	147.54	147.55
1	C5		145.7	146.59	147.54	147.55
1	Cl	127.2	125.8	126.57	126.79	126.81
1	Cl		124.6	126.57	126.79	126.81
1	Co	127.8	126.8	125.15	127.14	127.11
1	Co		129.9	129.54	127.92	128.00
1	Co		129.3	129.54	127.92	128.00
1	Cm	130.50	128.3	127.71	129.22	129.21
1	Cm		131.1	129.71	129.43	129.44
1	Cm		132.1	129.71	129.43	129.44
1	Cp	132.3	132.1	130.31	131.70	131.71
1	Me	11.2	9.2	9.74	10.63	10.64
1	Me		6.3	9.74	10.63	10.64
1	¹⁵ N1		-186.2	-191.51	-200.66	-200.81
1	¹⁵ N1		-187.4	-191.51	-200.66	-200.81
1	¹⁵ N2		-178.8	-182.19	-189.58	-189.74
1	¹⁵ N2		-180.8	-182.19	-189.58	-189.74
2	C3	148.0	145.1	146.05	147.93	147.96
2	C3		144.4	146.05	147.93	147.96
2	C4	105.7	101.9	102.06	105.19	105.06
2	C4		105.3	102.06	105.19	105.06
2	C5	148.8	146.2	147.08	148.14	148.23
2	C5	148.8	146.2	147.08	148.14	148.23
2	Cl	127.2	124.0	126.54	126.83	126.83
2	Co	127.8	125.7	125.60	126.95	126.86
2	Co		126.2	129.79	127.11	127.00
2	Co		127.3	129.79	127.11	127.00
2	Cm	130.5	128.3	128.15	129.59	129.59
2	Cm		132.0	129.51	130.02	130.10
2	Cp	132.3	130.5	130.52	131.51	131.54
2	Me	11.2	11.4	10.14	10.51	10.49
2	Me		9.5	10.14	10.51	10.49
2	¹⁵ N1		-188.4	-192.64	-199.60	-199.73
2	¹⁵ N1		-189.7	-192.64	-199.60	-199.73
2	¹⁵ N2		-184.6	-183.54	-191.42	-191.66
2	¹⁵ N2		-184.6	-183.54	-191.42	-191.66

Excluding the carbon atoms of the phenyl rings, the outliers for Eq. (2) were found, in the case of the pyrazolium chloride **1**, to be one of the methyl signals (6.3, fitted 10.3 ppm), one of the C4 signals (103.8, fitted 101.0 ppm) and both N1 signals (186.2 and 187.4, fitted 189.6 ppm). For the pyrazolium bromide **2**, one

Fig. 4. CPMAS experimental versus calculated chemical shifts for the gas-phase.

of the C4 signals (105.3, fitted 102.1 ppm) and the N2 signal (184.6, fitted 181.7 ppm). Note however, that the calculations reproduce the main differences between **1** and **2**.

These calculations reproduce some of the splittings observed in the solid state (Fig. 4), those corresponding to the *ortho* and *meta* carbon atoms of the phenyl rings. For instance the better agreement for the *ortho* and *meta* ¹³C signals can be explained by argument number (iii) discussed in the introduction: “the presence of restricted rotations and conformations that become free in solution because low barriers”, but certainly this explanation cannot be used to account for the fact that the *ipso* and *para* carbon signals are also split. This shows that there are other effects besides point (iii) that should be used to understand all the splittings observed in the experimental spectra.

Obviously, a C_2 structure cannot reproduce the properties of a $P2_1/n$ one because in a C_2 space group both pyrazolium rings are identical instead of being quite different (see Table 1).

b. Residual dipolar couplings (R.D.C.).

The presence of chlorine atoms on **1** and bromine atoms in **2** could produce splittings if they are close enough to the atoms

Fig. 5. Some distances (Å) between some atoms of **1** from the X-ray structure of SEGNIIB [2,3].

Table 5

Comparison between the experimental and QE-VC-Relax structural information of the SEGNIIB crystal.

P2 ₁ /n experimental	P2 ₁ /n final QE-VC-Relax structure
$a = 11.5274 \text{ Å}$	$a = 11.6802 \text{ Å}$
$b = 18.2559 \text{ Å}$	$b = 18.7710 \text{ Å}$
$c = 9.7001 \text{ Å}$	$c = 10.0354 \text{ Å}$
$\alpha = 90^\circ$	$\alpha = 90^\circ$
$\beta = 95.379^\circ$	$\beta = 96.856^\circ$
$\gamma = 90^\circ$	$\gamma = 90^\circ$
Volume = 2032.330 Å ³	Vol = 2184.342 Å ³

where the split was observed (Fig. 5). Although highly improbable, we wanted to calculate the R.D.C. to have a quantitative answer.

Residual couplings (D couplings) with the ³⁵Cl nuclei can be estimated using the interatomic distances from the nuclei where the split was observed to the ³⁵Cl nuclei, which are depicted in Fig. 5 for compound **1**. From this figure it can be observed that the distance between the carbon nuclei and any Cl nucleus is larger than 4 Å. Considering that Olivieri et al. [25] observed splittings of 5–6 ppm in 4-chloropyrazoles for ¹³C-³⁵Cl couplings between directly bonded atoms [26,27], and that the couplings are proportional to the inverse of the cube distance between the coupled nuclei, it is apparent that residual couplings with the Cl nuclei

cannot explain the large splittings observed in the SSNMR. Similar conclusions were drawn from a study of halogeno 1,2,4-triazoles [28].

c. Quantum Espresso (QE) calculations.

Due to practical limitations, QE calculations were restricted to compound **1**, but arguably these results should be transferable to compound **2** due to the close similarity of the solid state effects observed in both compounds (Table 3).

We have performed QE calculations starting from experimental crystal structure using the VC Relax option (P2₁/n symmetry group) using a kinetic energy cutoff = 65 Ry, which is comparable to the one used in previous calculations [29]. A new structure has been found by this optimization with the parameters reported in Table 5. The total energy of this structure is 493.049 Ry in comparison with a total energy of 492.084 Ry for the experimental structure. A difference of 0.96 Ry, which is 1268 kJ mol⁻¹. The new structure has a COMPAC RMS of 0.155 Å not including hydrogen atoms (Fig. 6a) and a RMS = 0.189 Å (Fig. 6b) including hydrogen atoms.

We performed also the QE calculation for the isolated dimer. We started from the dimer structure present in the experimental structure, and performed a relax QE optimization. We used a kinetic cutoff of 65 Ry, and used the same pseudopotentials

Fig. 6. Superposition of the calculated and experimental structures of compound **1**. (a) Not including hydrogen atoms. (b) Including hydrogen atoms.

Table 6

Calculated QE chemical shifts (σ , ppm) corresponding to the P2₁/n optimized structure. The calculated differences, in ppm, correspond to Mol. 1–Mol. 2.

Atom	Mol. 1	Mol. 2	Diff. (calc)	Diff. (exp)
C of CH ₃	158.40	162.29	−3.29	−2.9
C3	18.71	18.02	0.69	0.6
C4	56.42	61.35	−4.93	−3.6
C5	15.29	15.85	−0.56	0
C ipso	34.57	36.18	−1.61	−1.2
C ortho	32.57	34.45	−1.88	−0.6
C ortho	32.97	34.20	−1.23	−0.6
Between <i>ortho</i> C	−0.40	0.25	−0.65	−0.6
C meta	31.79	34.69	−2.90	−3.7
C meta	29.85	30.44	−0.59	−3.7
Between <i>meta</i> C	1.94	4.25	−2.31	−3.7
C para	30.00	29.27	0.73	0
N1	26.63	27.79	−1.16	−1.2
N2	18.36	16.01	2.35	2.0

employed in the VC *relax* optimization of the crystal structure, to compare the resulting chemical shifts for both systems. The final energy is 492.979 Ry; that respect to the initial structure taken from the starting dimer structure is 491.982 Ry. This means a difference of 0.997 Ry, which corresponds to 1317 kJ mol^{−1}.

The results with the isolated dimer (Table S2, Supplementary material) were unsatisfactory so we moved to the calculations taking into account the whole crystal based on its periodicity. The results are reported in Table 6. Contrary to comparisons between experimental chemical shifts, including those determined in the solid state (Fig. 4) that are increasingly common [30,31],

quantitative comparisons between experimental and calculated splittings have not been reported. There are several reasons: (i) obviously splitting due to differences in crystal geometries are observed only in SSNMR; (ii) the range of values is much smaller than in chemical shifts (see, for instance, Table 6, where the largest value is only 3.6 ppm); (iii) the assignment of the split signals to the different molecules present in the crystal is difficult [32].

We have assumed in Table 6 that the calculations for molecules 1 and 2 are correct and, thus, the signs of the experimental results are the same of the calculated ones. We have shown previously that the splitting of *ortho* and *meta* carbons (Table 4 and Fig. 4) is fairly well reproduced using a symmetric dimer. Now, we assumed that these splittings (0.6 and 3.7 ppm, Fig. 2) correspond to differences in the same molecule and not to differences between molecules. A plot corresponding to the data of Table 6 is represented in Fig. 7. The worse point corresponds to the *meta* carbons, the experimental value being 3.7 ppm and the calculated one 2.31 ppm; note that in Mol. 2, the *meta* carbons are separated 4.2 ppm, so probably in this case the splitting is mainly due to one molecule.

Conclusions

The main conclusions of the present work are:

- Large splittings are observed for some ¹³C and ¹⁵N SSNMR signals of 3(5) phenyl 5(3) methylpyrazolium halides.
- Extensive QM calculations of chemical shifts have been performed in an attempt to rationalize the splittings observed in SSNMR spectra of 3(5) phenyl 5(3) methylpyrazolium chloride.
- QE calculations successfully reproduce the large splittings observed by CPMAS NMR allowing a biunivocal and quantitative correspondence between the geometries determined by X ray crystallography and the chemical shifts obtained by SSNMR.
- Periodic theoretical calculations provide a link between two unrelated techniques, crystallography (electron density) and NMR (nuclei perturbed by electrons).

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molstruc.2014.07.020>.

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Fig. 7. Experimental versus calculated splittings. The regression line corresponds to experimental (ppm) = (0.86 ± 0.09) calculated (ppm), $n = 10$, $R^2 = 0.95$.

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