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# An excess electron binding to the ‘purple’ zwitterion quinonoid

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## Abstract

Zwitterionic and canonical isomers of a novel quinonoid species were studied using second-order Møller–Plesset perturbation theory with 6-31+G\*\*+5(sp)4d basis sets. An experimental report on the zwitterion being the most stable isomer was confirmed. In particular, the zwitterionic isomer is lower than the lowest canonical tautomer by 1.42 kcal/mol. Binding an electron to all isomers studied was considered, and the corresponding anionic species were studied. The lowest neutral isomer (zwitterion) forms a stable dipole-bound anion as do three out of four canonical isomers. However, the electron binding energy estimated for the zwitterion (521 cm<sup>-1</sup>) is the largest among all tautomers. © 2002 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The recent appearance of the experimental report [1] on an ‘unprecedented zwitterion in quinonoid chemistry’ (by Siri and Braunstein) attracted our attention due to our long interest in binding excess electrons to polar molecules [2–7]. Since 1999, we have been trying to find a molecular system for which the zwitterionic structure is relatively close in energy to its corresponding canonical isomer (tautomer) so that binding an extra electron renders the zwitterion-based anion thermodynamically more stable than the canonical-based anion. The idea we suggested was based on the observation that zwitterionic isomers, although less stable in the gas-phase, usually possess posi-

tive electron affinities because of their highly polar character. If such binding is strong enough to overcome the energy difference between the zwitterion and the canonical isomer, the zwitterionic structure could become the lowest-energy anionic structure in the gas-phase.

Recently, we undertook an extensive search for a neutral molecule having relatively small zwitterionic/canonical energy-gap, examining glycine [8], various isomers of arginine [9–11], urea [12], and betaine (as a model zwitterion system) [13]. Unfortunately, only for arginine did we conclude that attaching an excess electron provides an extra stabilization that equalizes the energies of the zwitterionic and canonical isomers (i.e., their electronic energies differ by less than 0.4 kcal/mol) [11]. For none of these systems, however, we were able to conclude that the excess electron binding renders the zwitterion the most stable in the gas phase.

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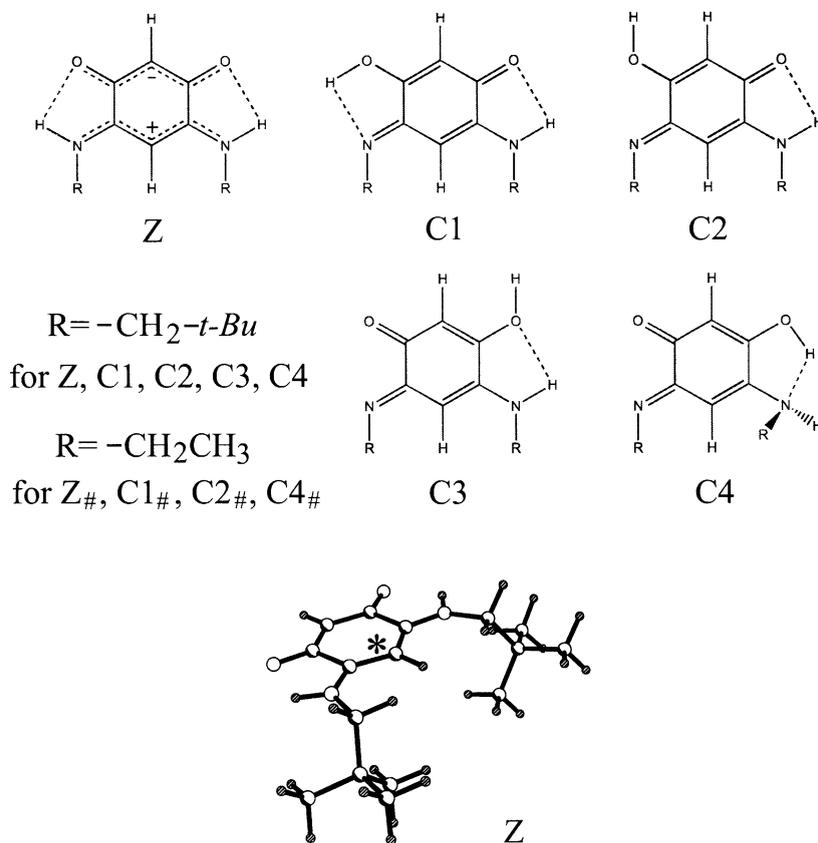


Fig. 1. Structural formulas of the zwitterionic and canonical species and the gas-phase equilibrium geometry structure of the lowest energy isomer (zwitterion).

The quinonoid molecule (**Z**) synthesized by Siri and Braunstein (see Fig. 1) provides a new hope for studying a thermodynamically stable zwitterionic system in the gas-phase [1]. This is the first  $12\pi$ -electron structure described in quinonoid chemistry in which, according to the authors, the positive charge is  $\pi$ -delocalized between the nitrogen atoms and the negative charge between the oxygen atoms [1]. Siri and Braunstein described **Z** as a ‘purple solid’ and they determined (via an X-ray diffraction study) its geometry to be planar, except for the  $-\text{CH}_2-t\text{-Bu}$  groups which both lie on the same side of the plane.<sup>1</sup> The UV–Vis ab-

sorption spectrum of **Z** (in  $\text{CH}_2\text{Cl}_2$ ) is characterized by two strong absorptions at 350 and 343 nm, which are claimed to correspond to the intraquinone charge transfers [1]. Species **Z** represents a novel electronic pattern for  $N,N,O,O$ -systems since previously known species of this kind display electronic delocalization exclusively between nitrogen and oxygen atoms with no occurrence of a zwitterionic structure [1,14]. In the case of **Z**, however, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra indicate the presence of the zwitterionic structure of  $\text{Z} \cdot 2\text{H}_2\text{O}$  and no evidence of a tautomeric equilibrium (i.e., the canonical isomer seems to be not present to any detectable extent) [1].

Although the successful synthesis of such a zwitterion **Z** opens several possibilities of utilizing it as a building block in coordination and

<sup>1</sup> An X-ray diffraction study was performed on single crystals of  $\text{Z} \cdot 2\text{H}_2\text{O}$  obtained from acetone/ $\text{H}_2\text{O}$ , see [1].

supramolecular chemistry, we became particularly intrigued by two issues: (i) if the thermodynamic stability of the zwitterion **Z** in the gas-phase can be confirmed by ab initio methods (it is well known that zwitterions, although less stable in the gas-phase, predominate in aqueous solutions) [15], and (ii) if an excess electron attachment to **Z** and its canonical isomer(s) leads to the situation in which the global-minimum on the anion ground-state potential energy surface (PES) corresponds to **Z**<sup>-</sup>.

In this contribution, we present our ab initio study on the neutral and anionic species **Z** and its four canonical isomers: **C1**–**C4** (see Fig. 1). In addition, we discuss the results obtained for a similar molecule **Z**<sub>#</sub> and its four canonical isomers **C1**<sub>#</sub>–**C4**<sub>#</sub> obtained by replacing the –CH<sub>2</sub>–*t*-Bu groups with ethyl groups (see Fig. 1).

## 2. Methods

The equilibrium geometries of the neutral species were optimized at the restricted Hartree–Fock (RHF) level with the 6-31+G\*\* basis sets [16] augmented with additional set of diffuse 5(sp) functions<sup>2</sup> (labeled 6-31+G\*\*+5(sp)) centered on the carbon atom marked with \* in Figs. 1 and 2. The harmonic vibrational frequencies were calculated at the same level of theory. For the smaller system **Z**<sub>#</sub> and its anion, we also performed geometry optimization at the MP2 level and verified that: (i) the neutral SCF and MP2 geometries have maximal bond length differences of 0.045 Å (both C–O bond lengths), and valence angle difference of 2.52° (for <CNH angle); (ii) other geometrical parameters differ by less than 0.025 Å (bond lengths) and 1° (valence angles); and (iii) attaching an extra electron to **Z**<sub>#</sub> causes even smaller geometry changes.<sup>3</sup> Therefore, we conclude that our SCF geometries of the neutral species are reliable and the calculated vertical electron attachment

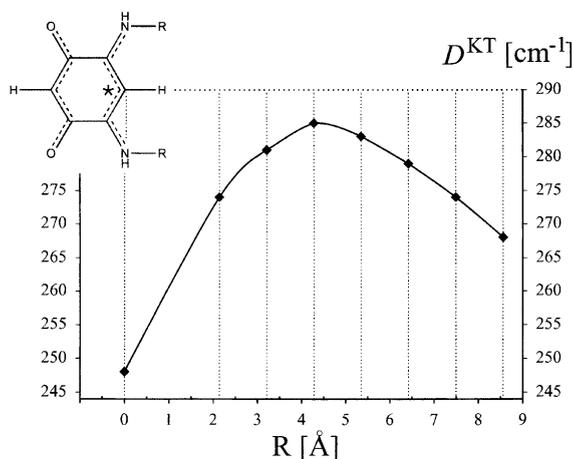


Fig. 2. Plot of the KT vertical electron binding energy of the **Z**<sup>-</sup> anion as a function of the distance separating the carbon atom marked with \* and the site where the additional 5(sp)4d set of diffuse functions was centered.

energies are likely close to the adiabatic electron affinities.

The electron binding energies (*D*) were calculated at the MP2 level<sup>4</sup> by subtracting the energies of the anion from those of the neutral. In addition, the dispersion ( $\Delta D_{\text{disp}}^{\text{MP2}}$ ) and non-dispersion ( $\Delta D_{\text{no-disp}}^{\text{MP2}}$ ) terms (the former describing the dispersion interaction between the loosely bound electron and the neutral molecule) were extracted from the MP2 contribution to *D*, as described elsewhere [5]. Since the electron binding energies were calculated in each case at the neutral's equilibrium geometry, they are vertical electron attachment energies (VAEs). Final electronic energies of all systems studied were determined at the second-order Møller–Plesset (MP2) perturbation theory level with the 6-31+G\*\*+5(sp)4d basis sets.

The 5(sp)4d diffuse set<sup>3</sup> was centered outside the molecule as to maximize the electron binding energy (*D*) at the Koopmans' theorem (KT) [17] level. In particular, we plotted the KT electron

<sup>2</sup> We used even tempered basis sets with the progression ratio equal to 3.2.

<sup>3</sup> The largest change in bond length is only 0.002 Å while the changes in valence angles are smaller than 0.4°.

<sup>4</sup> Because of the size of the systems studied and the necessity of employing relatively large basis sets to properly describe the excess electrons, we had to limit the level of our calculations to the MP2 level.

Table 1

Relative MP2/631+G\*\*+5(sp)4d energies of neutral and anionic species (see Section 2 for details) and SCF dipole moments of the neutral isomers

Isomer	Neutral	$\mu^{\text{SCF}}$	Anion
<i>R</i> = -CH <sub>2</sub> - <i>t</i> -Bu			
<b>C4</b>	1.126 (9080)	8.173	1.089 (8785)
<b>C3</b>	0.858 (6921)	7.095	0.841 (6785)
<b>C2</b>	0.545 (4399)	1.773	Unstable
<b>C1</b>	0.126 (1018)	4.793	0.122 (983)
<b>Z</b>	0.065 (521)	9.981	0.000 (0)
<i>R</i> = -CH <sub>2</sub> CH <sub>3</sub>			
<b>C4<sub>#</sub></b>	1.075 (8673)	8.253	1.016 (8196)
<b>C3<sub>#</sub></b>	0.902 (7274)	6.987	0.882 (7111)
<b>C2<sub>#</sub></b>	0.591 (4765)	2.174	Unstable
<b>C1<sub>#</sub></b>	0.136 (1095)	5.060	0.128 (1032)
<b>Z<sub>#</sub></b>	0.091 (735)	10.081	0.000 (0)

Energies in eV and cm<sup>-1</sup> (in parentheses), dipole moments ( $\mu^{\text{SCF}}$ ) in Debyes. For both species the energies are relative to the most stable anion.

binding energy ( $D^{\text{KT}}$ ) as a function of distance *R* separating the site where the 5(sp)4d diffuse set was centered and the carbon atom labeled \* in molecule **Z** (or **Z<sub>#</sub>**) (see Fig. 2). This plot shows that our choice of the centering site (*R* = 4.278 and 3.749 Å for **Z** and **Z<sub>#</sub>**, respectively) is optimal because it produces the strongest binding (although  $D^{\text{KT}}$  varies by only 37 cm<sup>-1</sup> over this range of *R*). We also verified that adding one more sp-diffuse shell to the 5(sp)4d set increases the  $D^{\text{KT}}$  value by less than 3 cm<sup>-1</sup>, while augmenting this set by one more d-symmetry shell leads to numerical instabilities caused by linear dependencies in the basis set. Additionally, we replaced the 6-31+G\*\*+5(sp)4d basis sets with the aug-cc-pVDZ+5s5p4d basis sets to determine whether the 6-31+G\*\* basis sets describe the neutral molecular core relatively well. Indeed, we found that  $D^{\text{KT}}$  changes by less than 10 cm<sup>-1</sup> (in the case of **Z**) when the latter basis set is used. Therefore, we conclude that any inaccuracies in our theoretical treatments are caused by the higher-than-second-order electron correlation effects rather than the basis sets employed.

All calculations were performed with the GAUSSIAN98 program [18] on Intel Pentium IV computers and an SGI Origin2000 numerical server. The three-dimensional plots of molecular orbitals were generated with the MOLDEN program [19].

### 3. Results and discussion

#### 3.1. Neutral zwitterionic and canonical species

Our MP2/6-31+G\*\*+5(sp)4d//SCF/6-31+G\*\*+5(sp) results (see Table 1) indicate that the zwitterion **Z** is indeed the lowest energy structure on the ground-state potential energy surface (PES) of the neutral (see Fig. 3). This suggests that this zwitterion is the most stable isomer even in the gas-phase, which is highly unusual. The canonical isomers (tautomers) (i.e., **C1**, **C2**, **C3**, and **C4**) are much higher in energy (by ca. 0.48–1.06 eV [11–25 kcal/mol]), except **C1** whose energy is but 0.061 eV (1.42 kcal/mol) above **Z**. This suggests that the zwitterionic **Z** and the canonical **C1** may both be present in the gas-phase. The kinetic barrier separating **Z** from **C1** was found to be 0.571 eV (13.17 kcal/mol) above **Z** at the MP2 level, so proton transfer from the nitrogen atom (in **Z**) to the oxygen (in **C1**) is not likely to occur easily.

That other canonical isomers (i.e., **C2**, **C3**, and **C4**) are significantly higher in energy is most likely caused by the possibility of making *two* internal hydrogen bonds in **Z** and **C1** versus *one* H-bond in **C2**, **C3**, and **C4** (see Fig. 1). Indeed, the energy gaps separating **Z** (or **C1**) and other structures (**C2**, **C3**, and **C4**), which is about 0.5–1 eV (11–25 kcal/mol), are consistent with the energy of a

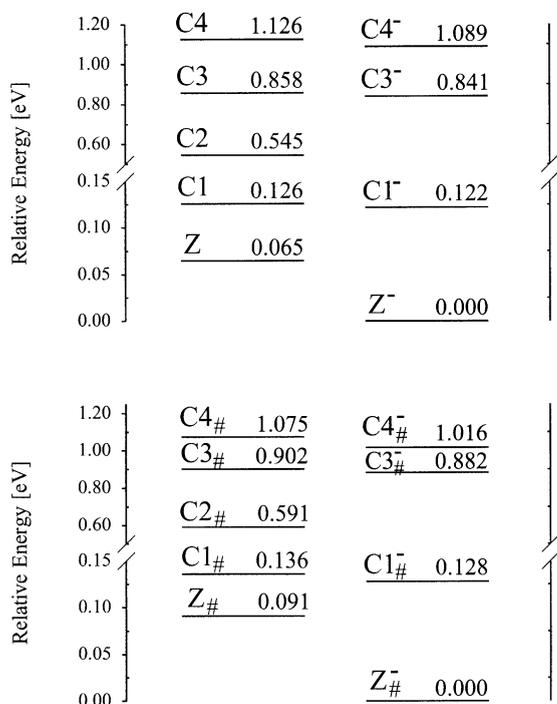


Fig. 3. Relative electronic MP2 energies (in eV and  $\text{cm}^{-1}$ ) of the minimum energy structures corresponding to the zwitterionic and canonical isomers of the quinonoid system with the  $-\text{CH}_2-t\text{-Bu}$  groups (top), and with the ethyl groups (bottom). The zero of energy is taken to be the energy of the lowest anion.

relatively strong hydrogen bond and differences in torsional energies.

A similar situation is observed for the system in which  $-\text{CH}_2-t\text{-Bu}$  is replaced by  $-\text{CH}_2\text{CH}_3$  (see Figs. 1 and 3). Here the zwitterion  $\mathbf{Z}_\#$  is also the lowest-energy neutral structure and the  $\mathbf{C1}_\#$  canonical isomer lies only 0.045 eV (1.03 kcal/mol) above  $\mathbf{Z}_\#$ . Other canonical isomers are separated from  $\mathbf{Z}_\#$  and  $\mathbf{C1}_\#$  by approximately 0.46–0.94 eV (10–22 kcal/mol), which is consistent with one less hydrogen bond being present in the latter structures.

As far as the charge distributions in the neutral structures are concerned,<sup>5</sup> both  $\mathbf{Z}$  and  $\mathbf{Z}_\#$  exhibit

relatively large charge separation and the charge-flow from the ‘lower’ to the ‘upper’ part of the molecule (that becomes negatively charged, see Fig. 1) can be estimated as  $0.6 e$  which confirms the zwitterionic character of these systems. This finding is consistent with the observation that the corresponding dipole moments of  $\mathbf{Z}$  and  $\mathbf{Z}_\#$  (ca. 10 D) are larger than those of the canonical tautomers (see Table 1).

Finally, in order to address the experimental report describing the UV–Vis absorptions of  $\mathbf{Z}$ , we performed a configuration interaction singles (CIS) calculation for  $\mathbf{Z}$ , focusing on transitions from the HOMO to low-energy valence excited orbitals. We did not consider transitions into dipole-bound orbitals because we were interested in simulating the results of [1] which involves a condensed phase where the dipole-bound orbitals are likely absent. According to our CIS results,  $\mathbf{Z}$  should absorb at 349 nm, while the measured spectrum [1] shows two strong absorptions at 350 and 343 nm. Since we precisely reproduced the former absorption but failed to find a nearby transition to be responsible for the latter, we speculate that the 343 nm band observed experimentally could be assigned to a vibrational excitation. The very small separation between these two bands (7 nm) lies in an energy range characteristic of soft vibrations. In Fig. 4, we show the HOMO, the dipole-bound orbital, and the valence-excited orbital of  $\mathbf{Z}$  to aid in the interpretation of the UV–Vis spectrum.

### 3.2. Attaching an excess electron to various tautomers

Our calculations indicate that all the tautomers studied (excluding  $\mathbf{C2}$  and its analog  $\mathbf{C2}_\#$ ) form electronically stable but weakly bound anions. The vertical electron attachment energies (Table 2) correlate well with the dipole moments of the neutral species (Table 1), thus it seems justified to characterize these anions as possessing dipole-bound nature.<sup>6</sup>

<sup>5</sup> The charge flow was estimated by calculating the partial atomic charges fitted to the electrostatic potential according to the Merz–Singh–Kollman scheme as described in B.H. Besler, K.M. Merz, Jr., P.A. Kollman, *J. Comput. Chem.* 11 (1990) 431.

<sup>6</sup> This statement greatly simplifies the conditions that have to be fulfilled to term an anion ‘dipole-bound’ – see [7] for details.

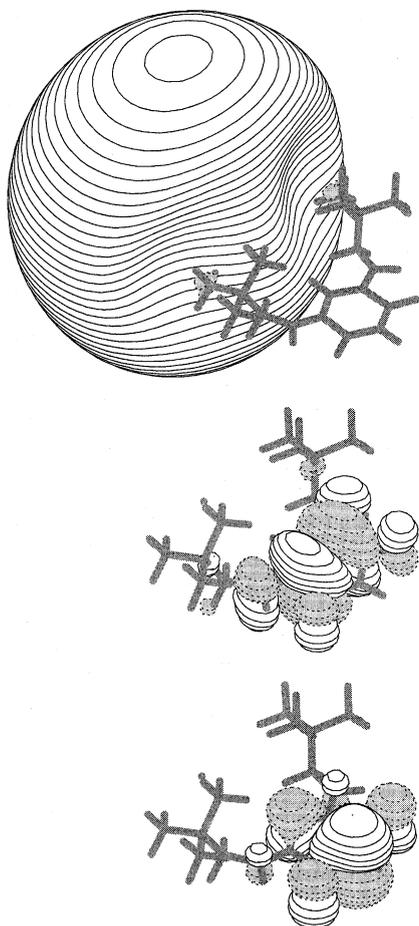


Fig. 4. The HOMO (bottom), valence-excited orbital, and dipole-bound orbital (top) of the lowest-energy **Z** species.

Let us briefly discuss various components of the calculated electron binding energies (Table 2).  $D^{\text{KT}}$  is responsible for ca. 30–60% of the total value of  $D$  in

all cases, and represents the electrostatic–exchange interaction of the excess electron with the charge density of the neutral molecule. The orbital relaxation effects included in  $\Delta D^{\text{SCF}}$  describe not only the static polarization of neutral structure by the loosely bound electron but also the effect of back-polarization. This contribution is small and represents less than 10% of the total electron binding energy. The dispersion term  $\Delta D_{\text{disp}}^{\text{MP2}}$  describes dynamical correlation between the loosely bound electron and the electrons of the neutral ‘core’. This term dominates the electron binding energy and is usually larger than  $D^{\text{KT}}$ , which is consistent with results for other dipole-bound anions [3–13]. Finally,  $\Delta D_{\text{no-disp}}^{\text{MP2}}$  is destabilizing and describes other electron correlation factors affecting the charge distribution (and the dipole moment) of the neutral molecule and thus its electrostatic interaction with the extra electron. However, the total MP2 contribution to  $D$  remains stabilizing due to the dominant role of the dispersion component. Our final predictions for the vertical electron attachment energies are  $521 \text{ cm}^{-1}$  for **Z** and  $735 \text{ cm}^{-1}$  for **Z**<sub>#</sub>, while the VAEs for canonical tautomers are smaller (see Table 2).

It is important to notice that the attachment of an extra electron provides differential stability to the zwitterionic structure **Z** (or **Z**<sub>#</sub>) relative to the canonical tautomers. As a consequence, the energy gap between the zwitterion **Z** (**Z**<sub>#</sub>) and the lowest-energy canonical tautomer **C1** (**C1**<sub>#</sub>) increases from 0.061 eV for **Z**/**C1** (0.045 eV for **Z**<sub>#</sub>/**C1**<sub>#</sub>) to 0.122 eV for **Z**<sup>-</sup>/**C1**<sup>-</sup> (0.128 eV for **Z**<sub>#</sub><sup>-</sup>/**C1**<sub>#</sub><sup>-</sup>) when the extra electron is attached (i.e., an increase of ca. 100%).

Analysis of the results obtained for systems possessing  $-\text{CH}_2-t\text{-Bu}$  groups or ethyl groups (see

Table 2

Components of the vertical electron attachment energies  $D$  (in  $\text{cm}^{-1}$ ) calculated with the 631+G\*\*+5(sp)4d basis sets

Species	$D^{\text{KT}}$	$D^{\text{SCF}}$	$D_{\text{disp}}^{\text{MP2}}$	$D_{\text{no-disp}}^{\text{MP2}}$	Sum ( $D^{\text{MP2}}$ )
$R = -\text{CH}_2-t\text{-Bu}$					
<b>C4</b>	156	20	178	-59	295
<b>C3</b>	68	7	72	-11	136
<b>C1</b>	11	2	26	-4	35
<b>Z</b>	285	36	253	-53	521
$R = -\text{CH}_2\text{CH}_3$					
<b>C4</b> <sub>#</sub>	277	41	279	-120	477
<b>C3</b> <sub>#</sub>	90	8	83	-18	163
<b>C1</b> <sub>#</sub>	31	2	38	-8	63
<b>Z</b> <sub>#</sub>	454	55	307	-81	735

Fig. 1) leads to the conclusion that the presence of the  $-\text{CH}_2-t\text{-Bu}$  groups is not crucial to the properties discussed here (e.g., the unusually high stabilization of the zwitterionic tautomer [even in the gas-phase] with respect to the canonical forms, and the ability to bind an excess electron and form electronically stable dipole-bound anions).

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