

Aromatic Ring Currents

Part I

The fact that the presence of aromatic rings in a sample preparation can be detected by signature chemical shifts in NMR spectra raises a surprisingly deep question. Although various advances have been made with NMR over many years e.g. continuous wave spectroscopy, etc., for the present purposes consider a sample in a time-constant, spatially uniform magnetic field in which the spatial extent of the sample is small compared to the region covered by the uniform field. Choose benzene as a representative aromatic molecule. Brownian motion will cause the benzene molecule to tumble vigorously in a liquid sample. However, ignore this motion and imagine that the benzene molecule is stationary, perhaps in a solid state preparation of some sort, and oriented with its plane perpendicular to the direction of the fixed magnetic field. The fact that the ^1H hydrogen atoms (and any ^{13}C carbon atoms) of this aromatic ring exhibit a chemical shift under these conditions implies that the ring has a persistent current that creates a magnetic moment that interacts with the spin magnetic moments of the benzene's hydrogen nuclei. In fact, this contribution adds to the effect of the external magnetic field as will be shown below (downfield or deshielded effect).

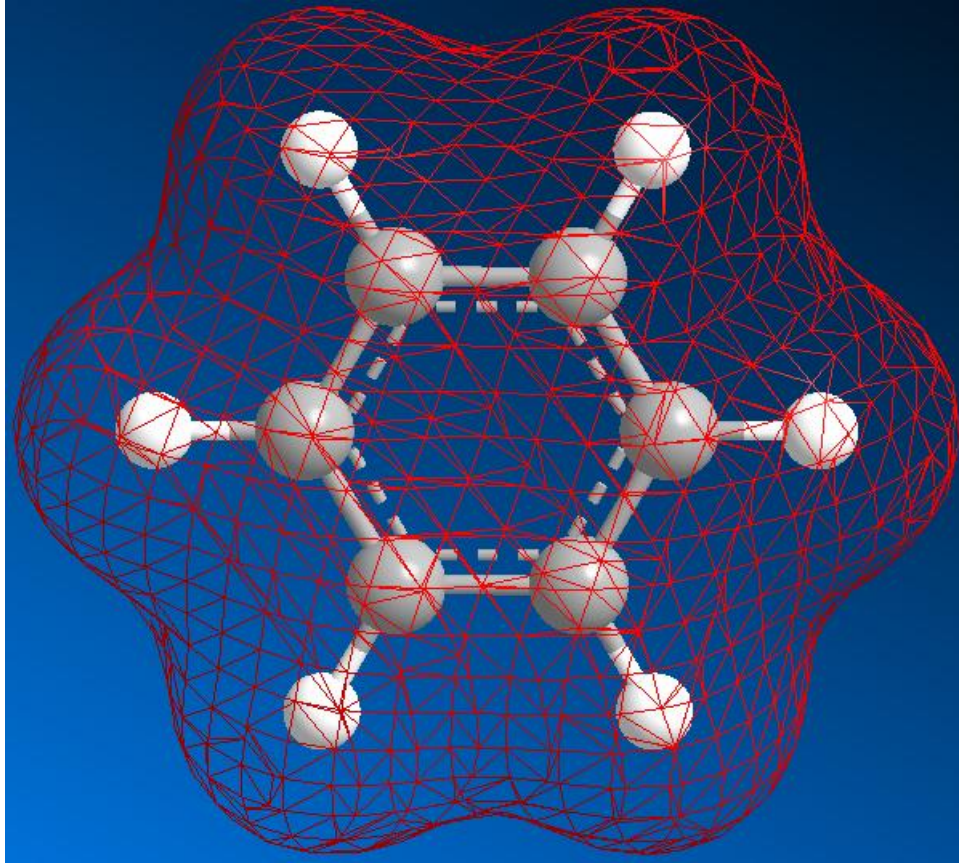
There are two main reasons this effect is a puzzle. The first reason has to do with macroscopic electromagnetism of conductor circuits and Faraday's law, Lenz' law and the effects of time-varying magnetic fields. These phenomena are captured by the Faraday's equation (in cgs units)

$$\vec{\nabla} \times \vec{E} = -\frac{1}{c} \frac{\partial \vec{B}}{\partial t}$$

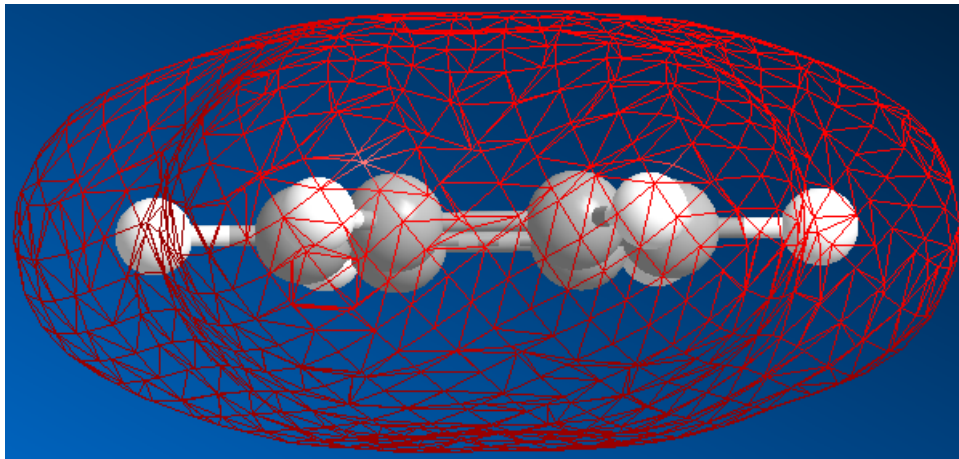
The minus sign is Lenz' law and this version of Faraday's law implies that a conducting loop exposed to a time-varying magnetic field that fluxes through the loop will develop an electric field along the loop, that in turn creates an electric current in the loop conductor. Such a current, of course, creates a magnetic field of its own that is directed so as to oppose the direction of the changing magnetic field that induced it. This was called diamagnetism by Faraday and still is. Thus, if a magnetic field that fluxes through a conducting loop is decreasing, the induced field in the region surrounded by the loop will tend to oppose this decrease. Moreover, if the time dependence of the magnetic field is eliminated, i.e. the field vanishes or becomes a time-constant field, the current will decay away to zero due to resistance and it will decay to zero very rapidly. How is this related to the benzene molecule in a magnetic field? The benzene molecule develops a ring current in a time-constant magnetic field !!

Currents in time-constant magnetic fields are not unprecedented. They occur in superconducting rings as well, where the electrical resistance is effectively zero (e.g. the resistance may decrease by, say, 16 orders of magnitude during the transition from normal conductivity to superconductivity). At low enough temperatures so that a ring is superconducting, a magnetic field that is initially present and then turned off will induce a ring current by Faraday's law. When the magnetic field is completely off and its source, an electromagnet, say, is removed far from the ring, the ring will continue to exhibit a persistent current for years !! This effect can be understood in terms of a macroscopic quantum state (quantum coherence) describing the state of the electrons in the superconducting ring. How is this related to the benzene molecule in a magnetic field? The benzene molecule develops a ring current even at room temperature and is not superconducting !!

The existence of a ring current in benzene, or any other aromatic molecule, when exposed to a time-constant, spatially uniform magnetic field can be understood as a quantum phenomenon (quantum coherence). To simplify the treatment as much as possible while preserving the essential details, benzene will be treated as a two dimensional circular disk with a radius of 3.0 angstroms (horizontal C-C distance of 2.8 Angstroms plus $2 \times$ C-H bond distances of 1.1 Angstroms plus 2×0.5 Angstrom extension beyond hydrogen atom). A quick look at a CPK model (or Bio3D plots) for benzene will confirm that the electron cloud of benzene is like a thick disk with no interior hole such as in a torus and unlike the impression made by a ball and stick model.



It is not as thick as it is wide.



The thickness will be ignored in the 2-d model but the lack of a hole will not. Thus, the model can be treated as a one electron problem for an electron attracted to a charged disk. This effectively models the π -electron cloud of real benzene. There are 6 such electrons in benzene. Our model is like solving the Schrodinger equation for a many electron atom as a one electron problem with the appropriate nuclear charge and then filling the eigenstates found with the correct number of electrons. Obviously one can be much more sophisticated and solve the many

electron problem directly but that would require a numerical approach and much insight would be lost.

The Hamiltonian for this one electron model is

$$H = \frac{1}{2m_e} \left(\vec{p} - \frac{e}{c} \vec{A} \right)^2 + V(\vec{r})$$

in which the charge of the electron, e , is intrinsically negative. The electric potential represents the attraction of the π -electrons for the charged disk. For the moment, all vectors are in 3-d. For a spatially uniform magnetic field the vector potential can be written

$$\vec{A} = \frac{1}{2} \vec{B} \times \vec{r}$$

wherein we choose the z-axis along the positive magnetic field direction, i.e.

$$\vec{B} = B \hat{k}$$

This means that the vector potential is in the x-y plane and circulates around the z-axis. It is elementary to show that the curl of this vector potential is equal to this magnetic field. The Schrodinger equation and its complex conjugate read as follows:

$$i\hbar \partial_t \psi = H\psi$$

and

$$-i\hbar \partial_t \psi = (H\psi)^*$$

The quantum probability density is defined by

$$\rho \equiv \psi^* \psi$$

Using the Schrodinger equation and its complex conjugate yields

$$i\hbar \partial_t \rho = i\hbar \left((\partial_t \psi^*) \psi + \psi^* (\partial_t \psi) \right) = -(H\psi)^* \psi + \psi^* H\psi$$

Since the scalar potential term, $V(\vec{r})$ is real, it cancels in the expression above, and it will no longer appear in the subsequent analysis. The remaining term of the Hamiltonian becomes

$$\left(\vec{p} - \frac{e}{c}\vec{A}\right)^2 = \left(-i\hbar\vec{\nabla} - \frac{e}{c}\vec{A}\right)^2 = -\hbar^2\nabla^2 + i\hbar\frac{e}{c}(\vec{\nabla}\cdot\vec{A} + 2\vec{A}\cdot\vec{\nabla}) + \frac{e^2}{c^2}A^2$$

Therefore

$$\begin{aligned} i\hbar\partial_t\rho &= -\frac{1}{2m_e}\psi\left(-\hbar^2\nabla^2\psi^* - i\hbar\frac{e}{c}(\vec{\nabla}\cdot\vec{A} + 2\vec{A}\cdot\vec{\nabla})\psi^* + \frac{e^2}{c^2}A^2\psi^*\right) \\ &\quad + \frac{1}{2m_e}\psi^*\left(-\hbar^2\nabla^2\psi + i\hbar\frac{e}{c}(\vec{\nabla}\cdot\vec{A} + 2\vec{A}\cdot\vec{\nabla})\psi + \frac{e^2}{c^2}A^2\psi\right) \\ &= -\frac{\hbar^2}{2m_e}(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*) + i\frac{\hbar e}{2m_e c}2(\psi\vec{A}\cdot\vec{\nabla}\psi^* + \psi^*\vec{A}\cdot\vec{\nabla}\psi) + \frac{\hbar e}{2m_e c}2\vec{\nabla}\cdot\vec{A}\psi^*\psi \\ &= -\frac{\hbar^2}{2m_e}(\psi^*\nabla^2\psi - \psi\nabla^2\psi^*) + 2i\frac{\hbar e}{2m_e c}\vec{\nabla}\cdot(\vec{A}\psi^*\psi) \\ &= -\frac{\hbar^2}{2m_e}\vec{\nabla}\cdot(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*) + 2i\frac{\hbar e}{2m_e c}\vec{\nabla}\cdot(\vec{A}\psi^*\psi) \end{aligned}$$

Therefore

$$\partial_t\rho = i\frac{\hbar}{2m_e}\vec{\nabla}\cdot(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*) + \frac{e}{m_e c}\vec{\nabla}\cdot(\vec{A}\psi^*\psi)$$

Since in general the probability density and the probability current density are related by

$$\partial_t\rho = -\vec{\nabla}\cdot\vec{j}$$

we conclude that the probability current density in this case is given by

$$\vec{j} = -i\frac{\hbar}{2m_e}(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*) - \frac{e}{m_e c}(\vec{A}\psi^*\psi)$$

Multiplication by e yields the electron current density

$$\vec{j}_e = -i\frac{\hbar e}{2m_e}(\psi^*\vec{\nabla}\psi - \psi\vec{\nabla}\psi^*) - \frac{e^2}{m_e c}(\vec{A}\psi^*\psi)$$

Clearly, the vector potential contributes to this electron current density. The minus sign reflects the diamagnetism. Since the magnetic field is positive along the positive z-axis, the vector

potential circulates around the positive z-axis in the right-handed sense. The minus sign reverses this current sense. This is all for an intrinsically positive current and reverse to the actual direction of electron motion. Such a positive current creates a magnetic field that points along the negative z-axis on the inside of the disk (i.e. at radii less than the disk radius). Outside the disk, of course, the magnetic field lines will have to reverse direction in order to circle back around the edge of the disk and back through the interior of the disk. This means that at radii larger than the disk radius, and in the plane of the disk, the magnetic field lines induced by the external field are parallel to that field. Since this is where the hydrogen nuclei of benzene are located, deshielding is the effect. Actually, as will be seen, this is also the direction of the induced magnetic field at the carbon atoms (deshielding).

Any apparent gauge dependence in this result because the vector potential appears is illusory. If we imagine a gauge change by a scalar field Λ

$$\vec{A} \rightarrow \vec{A} + \vec{\nabla}\Lambda$$

it will be compensated in the first term of \vec{J}_e by a corresponding gauge change to the wave function

$$\psi \rightarrow \psi e^{i\frac{e}{\hbar c}\Lambda}$$

The electric potential makes analytic solution of the Schrodinger equation impossible. Only numerical methods will work. The vector potential terms of the Hamiltonian create terms that depend on the external magnetic field strength. One can use cylinder coordinates to display the magnetic details of the Hamiltonian. The radial part of this representation (sans the electric potential) is

$$H = -\frac{\hbar^2}{2m_e} \left(\partial_r^2 + \frac{1}{r} \partial_r - \frac{m^2}{r^2} \right) + \frac{\hbar^2}{8m_e} \frac{r^2}{r_B^4} + m \frac{\hbar}{2} \omega_B$$

in which

$$r_B^2 \equiv \frac{\hbar c}{eB}$$

and

$$\omega_B \equiv \frac{eB}{m_e c}$$

Even for a magnetic field as large as 1 Tesla, r_B is over 200 Angstroms, i.e. much larger than the size of the benzene molecule. Consequently, these magnetic terms in the Hamiltonian can be treated as small perturbations. To calculate the vector potential contribution to the electric current we only need

$$-\frac{e^2}{m_e c} (\vec{A} \psi^* \psi)$$

which only requires a good estimate of the probability density $\psi^* \psi$.

We will now invoke the 2-d approximation and treat the probability density as two dimensional. This makes a current density that is appropriate in two dimensions as well. This means

$$\vec{K}(\vec{r}) = -\frac{e^2}{m_e c} \frac{1}{2} \vec{B} \times \vec{r} \psi^* \psi$$

wherein

$$\psi^* \psi = \frac{1}{\pi r_0^2}$$

with $r_0 = 3$ Angstroms. Note that the units of this density are reciprocal area as is required for a 2-d treatment. That means the units (cgs) for the current density, \vec{K} , are esu/s-cm. This current density creates a magnetic moment given by (cgs units)

$$\begin{aligned} \vec{m} &= \frac{1}{2c} \int_0^{2\pi} d\varphi \int_0^{r_0} r dr \vec{r} \times \vec{K}(\vec{r}) = -\frac{e^2 B}{4m_e c^2} \int_0^{2\pi} d\varphi \int_0^{r_0} dr r^3 \frac{1}{\pi r_0^2} \hat{k} \\ &= -\frac{e^2 B r_0^2}{8m_e c^2} \hat{k} \end{aligned}$$

In cgs units, the B coefficient is of magnitude

$$\frac{e^2 r_0^2}{8m_e c^2} = 3.2 \times 10^{-29} \text{ cm}^3$$

Since the cgs units for B are esu/cm², the magnetic moment's units work out to be esu-cm (\equiv erg/gauss = 10⁻³ J/T), as expected. Note that the direction of this magnetic moment is along the

negative z-axis, as expected for diamagnetism. The magnetic field induced anywhere in the plane of the benzene depends on the distance from the center, where the effective magnetic moment resides, and is given for this 2-d geometry by

$$\vec{B}_{induced} = -\frac{\vec{m}}{r^3}$$

This reinforces the external field and is proportional to the strength of the external field. Thus the effect can be expressed as a chemical shift that is independent of external field strength. The hydrogens are located 2.5 Angstroms from the center. Thus the effect is proportional to the external field strength with a proportionality given by

$$\frac{|\vec{m}|}{(2.5 \times 10^{-8})^3 B} = \frac{3.2 \times 10^{-29}}{15.63 \times 10^{-24}} = 2 \times 10^{-6}$$

This is 2 ppm per electron. For 6 π -electrons, we get ~12 ppm. The order of magnitude is right on! For ^{13}C nuclei, the distance is less, equal to 1.4 Angstroms, but the effect is of the same nature, i.e. deshielding. The chemical shift's magnitude for ^{13}C compared to ^1H is 5.7 times bigger. While these results are ball-park, the crudeness of the model prevents them from being quantitative.

Part II

In the part I of this analysis, the electron density for a benzene ring was approximated as a circular distribution in the x-y plane with radial dependence only. The vector potential contribution to the current was calculated by first calculating the magnetic dipole moment of the distribution and then using that in the formula for a magnetic field created by a magnetic dipole. Such a procedure is valid if the resulting magnetic field is determined for distances from the center of the electron distribution that are large compared to the extent, r_0 , of the electron distribution. This is not the case for distances corresponding to the the location of ^1H protons and ^{13}C nuclei in benzene (r_0 was taken to be 3 angstroms, the distance to ^1H was 2.5 angstroms and the distance to ^{13}C was 1.4 angstroms). Thus the results obtained were only order of magnitude but not quantitative. Nevertheless, the results were in the observed ball park of chemical shifts for benzene. It is possible to do the electromagnetic part of this calculation much better since the formula for the magnetic field anywhere in space resulting from a circular current loop with current I is well known and readily found in text books.

For a circular current loop in the x-y plane with current I in the right-handed sense around the z-axis, the resulting magnetic field *in the x-y plane* is solely along the z-axis, with

vanishing radial and azimuthal components. In cgs units the magnetic field at distance r for a circular loop of radius r' is given by

$$B(r) = \frac{I}{c} \pi (r')^2 \sum_{n=0}^{\infty} \frac{(-1)^n (2n+1)!!}{2^n (n+1)!} \left\{ \begin{array}{l} -\left(\frac{2n+2}{2n+1}\right) \frac{1}{(r')^3} \left(\frac{r}{r'}\right)^{2n} \\ \frac{1}{r^3} \left(\frac{r'}{r}\right)^{2n} \end{array} \right\} P_{2n+1}^1(0)$$

in which the upper formula is for $r < r'$ and the lower formula is for $r' < r$. The associated Legendre polynomials are given by

$$P_{2n+1}^1(0) = \frac{2\sqrt{\pi}}{\Gamma(n+1)\Gamma\left(-n-\frac{1}{2}\right)} = (-1)^{n+1} \frac{(2n+1)!!}{2^n n!}$$

because

$$\Gamma(n+1) = n!$$

and

$$\Gamma\left(-n-\frac{1}{2}\right) = \Gamma\left(\frac{1}{2} - (n+1)\right) = \frac{(-1)^{n+1} 2^{n+1} \sqrt{\pi}}{(2n+1)!!}$$

Using the surface current density from part I of this presentation

$$K(r') = -\frac{e^2 B}{m_e c} \frac{1}{2} r' \frac{1}{\pi r_0^2}$$

the current of a ring at r' with width dr' is given by

$$I = K dr'$$

Therefore the contribution of this bit of ring current to the magnetic field is given by

$$dB = \pi (r')^2 \left(-\frac{e^2 B}{m_e c^2} \frac{1}{2} r' \frac{1}{\pi r_0^2} \right) dr' \sum_{n=0}^{\infty} \frac{(-1)^n [(2n+1)!!]^2}{2^{2n} (n+1)! n!} \left\{ \begin{array}{l} -\left(\frac{2n+2}{2n+1}\right) \frac{1}{(r')^3} \left(\frac{r}{r'}\right)^{2n} \\ \frac{1}{r^3} \left(\frac{r'}{r}\right)^{2n} \end{array} \right\}$$

$$= \pi \left(-\frac{e^2 B}{m_e c^2} \frac{1}{2\pi r_0^2} \right) \sum_{n=0}^{\infty} \frac{(-1)[(2n+1)!!]^2}{2^{2n}(n+1)!n!} \left\{ \begin{array}{l} -\left(\frac{2n+2}{2n+1}\right) \left(\frac{r}{r'}\right)^{2n} \\ \frac{(r')^3}{r^3} \left(\frac{r'}{r}\right)^{2n} \end{array} \right\} dr'$$

For $0 < r < r_0$, which is appropriate for the location of ^1H or ^{13}C , the magnetic field is given by

$$B(r) = \int_0^r dB_{lower} + \int_r^{r_0} dB_{upper}$$

Before evaluating these integrals, note that the three minus signs for the upper formula imply a magnetic field that points down the negative z-axis, as is appropriate inside a current ring, whereas the two minus signs for the lower formula imply a positive magnetic field as would be appropriate outside a current ring. This is the intrinsic diamagnetism. For ^1H , most of the current is inside the radius where the ^1H is located whereas for ^{13}C nearly half the current is outside the radius where the ^{13}C is located. The integrations are elementary and the resulting expression needs to be evaluated numerically for the two cases of ^1H and ^{13}C . The location of ^{13}C relative to ^1H greatly decreases the effect on ^{13}C , unlike the result for the magnetic dipole approximation given in part I. It is also noted that this result is for one π -electron and there are six. Furthermore, if r is much larger than r_0 then the integral over the lower formula alone is correct and is dominated by the $n = 0$ term. This term gives precisely the value obtained in the dipole approximation of part I.

To do an even better evaluation, a better approximation to the electron density must be used (it is not circularly symmetric but hexagonally symmetric as is seen in the figure of part I). The thickness of this density should also be included. These refinements will improve the quantitative results but not the qualitative nature of the analysis. For that reason, further pursuit of more precise chemical shifts is not done here.

Part III

The integrals of part II easily give a formula for the magnetic field, in the plane of the disk representing the benzene ring, and at radius $r < r_0$ that is

$$B(r) = \frac{e^2 B}{2m_e c^2 r_0^2} \sum_{n=0}^{\infty} \frac{[(2n+1)!!]^2}{2^{2n}(n+1)!n!} \left\{ \frac{1}{2n+4} r - \frac{2n+2}{(2n+1)(2n-1)} \left(r - \frac{r^{2n}}{r_0^{2n-1}} \right) \right\}$$

This summation is very slowly convergent and requires care to compute. For benzene, $r_0 = 3 \text{ \AA}$. The hydrogen protons are located at $r = 2.5 \text{ \AA}$ and the carbon (^{13}C) nuclei are located at $r = 1.4 \text{ \AA}$. Writing the result in four factors

$$B(r) = B \left(\frac{e^2}{m_e c^2 r_0} \right) \frac{1}{2r_0} \Sigma$$

wherein Σ represents the summation, it is found that

$$\Sigma = \begin{cases} -0.538 r_0 & \text{for } r = 2.5 \text{ \AA} \\ -1.648 r_0 & \text{for } r = 1.4 \text{ \AA} \end{cases}$$

and that

$$\left(\frac{e^2}{m_e c^2 r_0} \right) = 0.948 \times 10^{-5}$$

which is dimensionless. This implies that the chemical shift for ^1H caused by 6 π -electrons is

$$-6 \times 0.948 \times 10^{-5} \times 0.5 \times 0.538 = -15.3 \text{ ppm}$$

and that for ^{13}C is

$$-6 \times 0.948 \times 10^{-5} \times 0.5 \times 1.648 = -46.9 \text{ ppm}$$

The first is about 2 times too big, and the second needs to be compared to a reliable source, so far not identified. The value for hydrogen is similar to the value found using the dipole approximation, even a bit larger. The value for carbon, however, is reduced, as is expected since the dipole approximation should be worse for an interior nucleus. Since a uniform electron density on a 2-d disk was used to model benzene's actual electron density, a better result would utilize a more accurate electron density. The result does show that the persistent electron current in an aromatic ring caused by a time-constant external magnetic field is a result of quantum coherence, and yields chemical shifts that are nearly quantitative.

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