

Molecular Ordering of a Nematic Liquid Crystal in a Dielectric Medium

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A computational analysis of the molecular ordering of 4-(4'-ethoxyphenylazo) phenyl hexanoate (**EPPH**) has been carried out on the basis of intermolecular interaction energy calculations. The **CNDO/2** method has been employed to evaluate the net atomic charge and atomic dipole moment components at each atomic centre of the molecule. A modified Rayleigh-Schrödinger perturbation theory along with a multicentered-multipole expansion method has been employed to evaluate long-range intermolecular interactions, while a "6-exp" potential function has been assumed for short-range interactions, and corresponding probabilities have been calculated in a dielectric medium (benzene) using the Maxwell-Boltzmann formula. Further, the flexibility of various configurations has been studied in terms of variations of the probability due to departure from the most probable configuration. All possible geometrical arrangements between molecular pairs have been considered during stacking, in-plane and terminal interactions, and the most favourable configuration of the pairing has been obtained. It has been observed that in a dielectric medium the probabilities are redistributed and there is a considerable rise in the probability of interactions although the order of preference remains the same. An attempt has been made to explain the nematogenic behaviour of liquid crystals and thereby develop a molecular model for liquid crystallinity. Results have been discussed in the light of those obtained for other nematogens like **EPPV** [4-(4'-ethoxyphenylazo) phenyl valerate] and **DPAB** [4-4'-di-*n*-propoxy-azobenzene].

Key words: CNDO/2 Method; Intermolecular Interactions; Statistical Analysis; Computer Simulation.

Introduction

Theoretical studies on the role of intermolecular forces in the mesomorphic behaviour have attracted the attention of many workers [1–5]. It has been argued that detailed analysis of pair interactions between the molecules of crystal lattices is expected to offer a better understanding of the mesomorphism [6]. Tokita et al. [7] used the Lennard-Jones potential to evaluate intermolecular interactions between a couple of pure nematogens and attempted to correlate their results with those of molecular field theory. However, it has been observed that the '6-exp' type of potential functions is more effective in explaining the molecular packing instead of the Lennard-Jones potential [8].

Inspired by the success of Tokita et al. [7], Sanyal et al. [9–11] and Tiwari et al. [12] improved the method and, taking a Buckingham potential with modified Rayleigh-Schrödinger perturbation theory, evaluated the interaction energy of molecular pairs. In these calculations, the energy was optimized with respect to various possible configurations, and ultimately a stable molecular packing geometry was obtained. Attempts were also made to correlate the mesogenic properties with molecular inter-

actions. The interaction energies for pairs of mesogens reported in the literature indicate the preference of a particular configuration over others, depending on their energy values. These values, however, do not reflect the actual relative preference, which can only be obtained through the probabilities corresponding to each configuration.

Since mesogenic properties are related to molecular aggregation in a specific manner, probability calculations based on energy distribution results will provide information regarding the most probable molecular aggregation.

Liquid crystalline materials are known for their anomalous physical properties near phase transitions. Molecular ordering of liquid crystals in solution (i.e. non-polar solvent benzene) has been studied by Sanyal et al. [13–16] using various techniques. It has been observed that the intermolecular interactions rise considerably in dielectric media. In order to confirm these experimental findings, we have decided to study theoretically the probability distribution of a homomolecular pair of liquid crystalline molecules in a dielectric medium (benzene). The dielectric constant of benzene has been taken to be 2.25 in the entire temperature range [16].

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In the present paper, an attempt has been made to interpret the statistical distribution (based on intermolecular interaction energy calculations) of a pair of **EPPH** (see the abstract) molecules at a distance of 6 Å for stacking and 8 Å for planar interactions in a dielectric medium. Similarly, a distance of 24 Å has been kept for terminal interactions. The choice of the distance has been made to eliminate the possibility of van der Waals contacts and to keep the molecule within the range of short and medium range interactions. A possible explanation of the liquid crystallinity of **EPPH** has been furnished. Results are compared with the those obtained for other nematogens like **EPPV** [17] and **DPAB** [18] (see the abstract).

An examination of thermodynamic data shows that **EPPH** becomes nematic at 348 K and isotropic at 399 K [19].

The computations have been carried out by keeping one molecule fixed in the *XY*-plane and placing the other molecule on both sides during stacking, in-plane and terminal interactions.

Computational Details

Computations have been carried out in two parts:

(A) The **CNDO/2** method [20] has been employed to compute the net atomic charge and dipole moment at each atomic centre of the molecule. According to second order perturbation theory as modified for intermediate range [21], the interaction energy (E_{total}) between a pair of molecules is given by

$$E_{\text{total}} = E_{\text{el}} + E_{\text{pol}} + E_{\text{disp}} + E_{\text{rep}},$$

E_{el} , E_{pol} , E_{disp} , and E_{rep} representing the electrostatic, polarization, dispersion, and repulsion energy, respectively. The electrostatic energy has been evaluated as the sum of various multipole-multipole interactions acting at different atomic centres as follows:

$$E_{\text{el}} = E_{\text{QQ}} + E_{\text{QMI}} + E_{\text{MIMI}} + \dots,$$

where E_{QQ} , E_{QMI} , and E_{MIMI} are the monopole-monopole, monopole-dipole and dipole-dipole terms, respectively. In general, for most of the molecular systems the evaluation of the electrostatic energy up to the dipole-dipole term has been found to be adequate [22].

In the present work the dispersion and short-range repulsion terms are considered together because several semiempirical approaches, viz. the Lennard Jones or Buckingham type approach, actually proceed in this way [23]. Kitaigorodskii introduced a Buckingham formula

whose parameters were later modified by Kitaigorodskii and Mirskay for hydrocarbon molecules and several other molecules [23].

(B) The total energies obtained from these computations were used to calculate the probability of each configuration in the dielectric medium using the Maxwell-Boltzmann formula [24].

$$P_i = e^{-\beta \epsilon_i} / \sum_i e^{-\beta \epsilon_i},$$

where P_i is the probability, $\beta = 1/kT$, and ϵ_i represents the energy of the configuration i relative to the minimum energy value in a particular set for which the probability distribution is computed. The details of the formulae may be found in [17, 18, 25, 26].

Crystallographic data from the literature have been used to construct the molecular geometry of the **EPPH** molecule with standard values of bond lengths and bond angles. The phenyl rings are planar but not coplanar, the angle between two normals being 10.16° [19].

Energy minimization has been carried out for stacking, in-plane and terminal interactions. One of the interacting molecules is kept fixed while lateral and angular variations are introduced for the other one relative to the fixed one. An accuracy of 0.1 Å in translation and 1° in rotation has been achieved. The origin has been chosen close to the centre of mass of the molecule, the *X*-axis along a bond parallel to the long molecular axis, the *Y*-axis in the plane of the molecule and the *Z*-axis perpendicular to the *XY* plane.

All computations were carried out with a program for a CDC 'Cyber-170' computer.

Results and Discussion

The molecular geometry of **EPPH** is shown in Figure 1. Table 1 represents a comparison of the total energy, the binding energy and the total dipole moments of **EPPH** with other nematogens like **DPAB** and **EPPV**. Evident by the total energy and the total binding energy of these molecules exhibit the order

$$\mathbf{EPPH} > \mathbf{EPPV} > \mathbf{DPAB},$$

while the total dipole moments exhibit the order

$$\mathbf{EPPH} > \mathbf{DPAB} > \mathbf{EPPV}.$$

The probabilities of different interacting configurations in a dielectric medium (benzene) are discussed below.

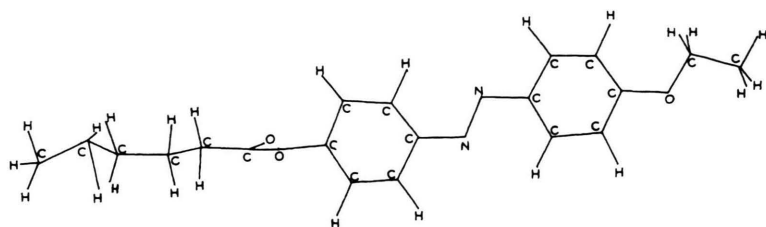


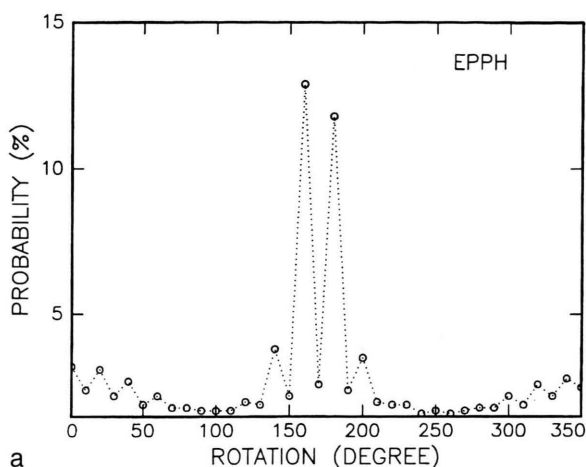
Fig. 1. Molecular geometry of 4-(4'-ethoxyphenylazo) phenyl hexanoate.

Table 1. Calculated total energy, binding energy and total dipole moment of **EPPH**, **DPAB** and **EPPV** molecules using the **CNDO/2** method.

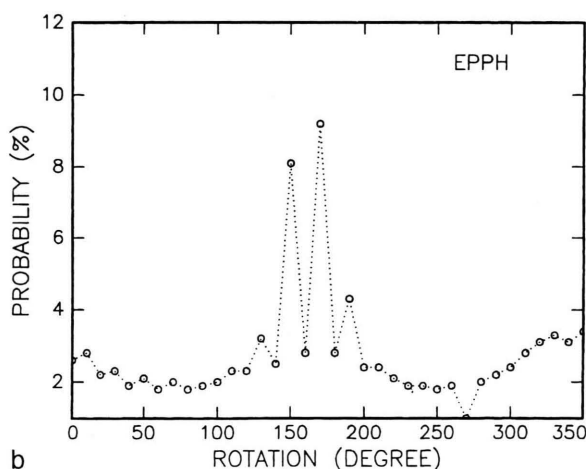
Molecule	Total Energy (a.u.)	Binding Energy (a.u.)	Dipole Moment Components (Debye)			
			μ_X	μ_Y	μ_Z	μ
EPPH	-239.23	-24.20	-0.49	1.27	-0.89	1.64
DPAB	-223.57	-22.15	-1.01	0.57	0.89	1.46
EPPV	-230.56	-22.96	-0.39	-0.29	-0.47	0.68

Stacking Interactions

The interacting molecule was placed at a separation of 6 Å along the Z-direction with respect to the fixed one. Rotations about the Z-axis are given at intervals of 10° and the corresponding probabilities were calculated. Figures 2a and 2b show the results obtained for rotations about the Z-axis with X (0°) Y (0°) and X (180°) Y (0°) configurations, respectively. These figures reveal that the maximum probability for X (0°) Y (0°) occurs at 160° while that for X (180°) Y (0°) occurs at 170°, indicating a preference for aligned structure in this configuration. The probability of perpendicular stacking is almost negligible, as expected. Having refined the interacting configurations with respect to translation along the Z-axis and rotation about the Z-axis at equilibrium, the energy is brought down and the probability is further investigated with respect to translation along the X-axis (Figure 3). Sharp maxima corresponding to the minimum energy point with more than 15% probability occur at the nematic – isotropic transition temperature. The variation of the probability is almost constant for the region (14 ± 6) Å near the equilibrium position, which shows that a sliding of one molecule over the other is energetically allowed for a small range which may be correlated with the fluidity if the compound maintains its alignment in the mesophase. Details of the variation of the probability with respect to rotation about the X-axis are shown in Fig. 4 corresponding to configuration Y (0°) Z (0°). A maximum in the probability is observed near the equilibrium



a



b

Fig. 2. Variation of the probability with respect to rotation about the Z-axis during stacking interactions at 399 K in a dielectric medium; 2a: corresponding to the configuration X (0°) Y (0°), 2b: corresponding to the configuration X (180°) Y (0°).

position. Table 5 shows the rotational rigidities along the X, Y, and Z-axis. It may be observed that the rotational rigidity about the long molecular axis during stacking interaction is 0.56 at the nematic – isotropic transition temperature. However, at room temperature the value is 0.58, indicating a strong binding at lower temperature.

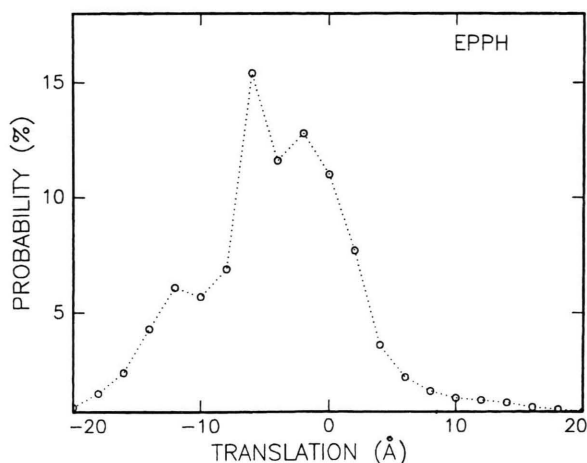


Fig. 3. Variation of the probability with respect to translation along X-axis during stacking interactions at 399 K in a dielectric medium.

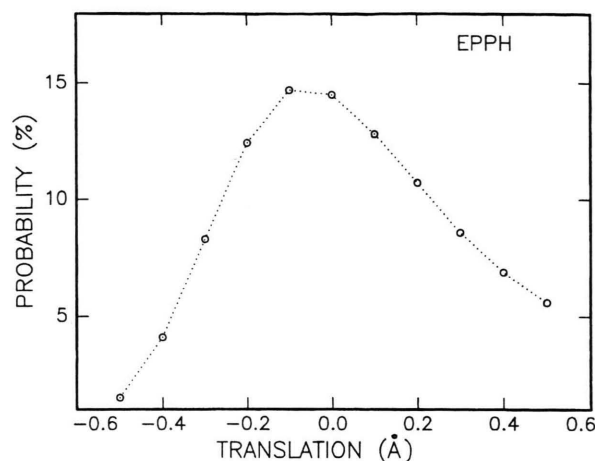


Fig. 5. Variation of the probability with respect to translation along the Z-axis during stacking interactions in a dielectric medium.

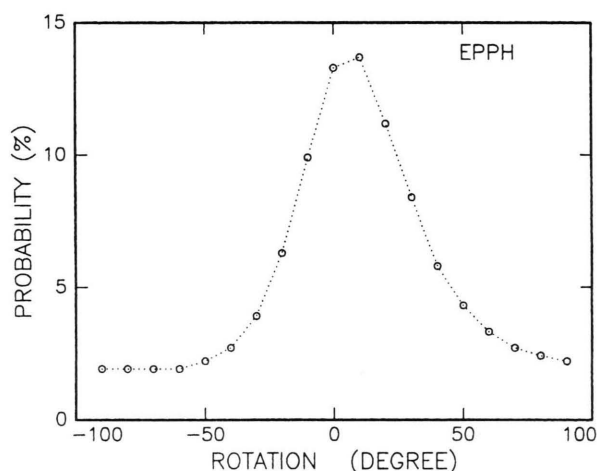


Fig. 4. Variation of the probability with respect to rotation about the X-axis during stacking interactions at 399 K in a dielectric medium.

With the increase of temperature the molecules obtain sufficiently freedom to rotate about the long molecular axis.

The effect of translation along Z-axis is shown in Fig. 5, where it may be observed that minor translations along the Z-axis do not alter the total energy and probability distribution drastically.

In-plane Interactions

Similar calculations have been performed for planar interactions of the molecule at an intermediate separa-

Table 2. Comparative picture of rotational rigidities along the X, Y-, and Z-axis corresponding to the most probable configuration during stacking and in-plane interactions between a pair of **EPPH** molecules in a dielectric medium benzene.

Temperature (K)	Rotational Rigidities		
	Stacking Interactions		In-plane Interactions
	About Z-axis	About X-axis	About Y-axis
300	4.68	0.58	0.57
399*	2.69	0.56	0.55
450	2.20	0.55	0.54

* Nematic – Isotropic Transition Temperature

tion of 8 Å. Figure 6 shows the results with respect to translation along the long molecular axis. It may be observed that the translation freedom is much more pronounced than that of the stacking interactions.

Figure 7 shows the results corresponding to the rotation about the Y-axis. It is clear that there is no drastic preference for the aligned structure; the smooth rise near 150° and 170° indicates the existence of an aligned structure at low temperature when the thermal agitation does not drastically disturb the molecular alignment.

Terminal Interactions

Since the length of molecule is approximately 22 Å, to investigate the terminal interaction away from the van

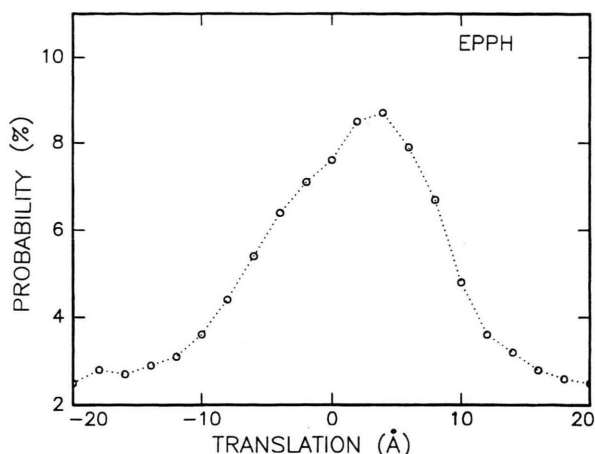


Fig. 6. Variation of the probability with respect to translation along *X*-axis during inplane interactions at 399 K in a dielectric medium.

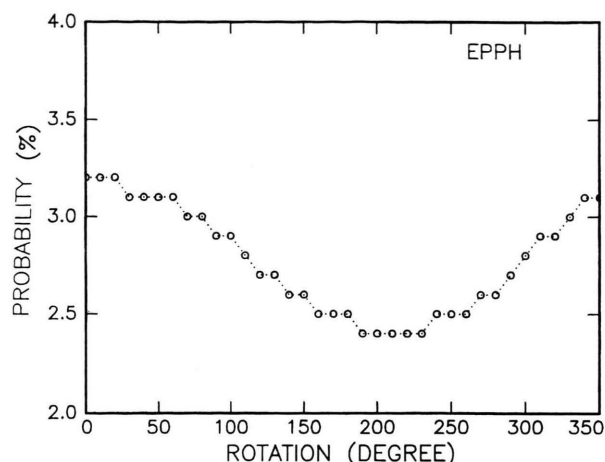


Fig. 8. Variation of the probability with respect to rotation about *X*-axis during terminal interactions at 399 K in a dielectric medium.

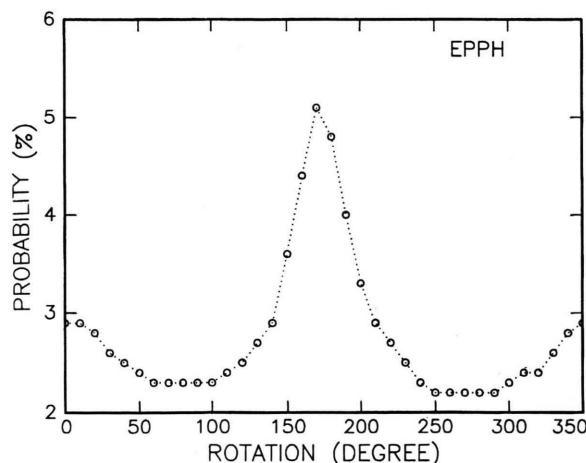


Fig. 7. Variation of the probability with respect to rotation about *Y*-axis during inplane interactions at 399 K in a dielectric medium.

Table 3. Stacking, in-plane and terminal interaction energies between a molecular pair of **EPPH** molecules after refinement. Energy is expressed in kcal/mole.

Interaction Energy Terms	Stacking Energy		In-plane Energy		Terminal Energy	
	+6 Å	-6 Å	+8 Å	-8 Å	+24 Å	-24 Å
E_{QQ}	-0.154	0.039	-0.036	0.023	0.003	0.010
E_{QMI}	-0.468	0.056	-0.126	-0.000	-0.043	-0.015
E_{MIMI}	-0.393	0.636	0.018	0.036	0.031	-0.016
E_{el}	-1.015	0.731	-0.144	0.058	-0.009	-0.021
E_{pol}	-0.325	0.278	-0.096	-0.123	-0.011	-0.016
E_{disp}	-8.925	-8.766	-5.649	-5.246	-2.267	-2.569
E_{rep}	3.933	1.018	2.139	2.034	1.228	0.995
E_{total}	-6.332	-7.017	-3.749	-3.277	-1.059	-1.610

der Waals contacts the interacting molecule has been shifted along the *X*-axis by 24 Å with respect to the fixed one, and rotations about the *X*-axis were given and corresponding probabilities reported. Rotations about the *X*-axis (Fig. 8) show absolutely no preference for any angle i.e. the molecules are completely free to rotate about their long molecular axis.

The most prominent energy minima of the above mentioned interactions are further refined with an accuracy of 0.1 Å in translation and 10° in rotation, and the values thus obtained are listed in Table 3 with all the con-

tributory terms to enable comparison. The results indicate that the refinement corresponding to the stacking energy is maximum, and the ultimate magnitude of the stacking energy is much larger than the in-plane and terminal interaction energy. Table 4 shows the relative probabilities of different minimum energy configurations calculated theoretically in vacuum and in dielectric medium. It may be observed that in the dielectric medium the probabilities are redistributed and there is a considerable rise in the probabilities of interactions, although the order of preference remains the same. Further, the configuration *Y*(0°) *Z*(0°) has maximum relative probability (87.8%) at room temperature (300 K) with an energy - 6.024 kcal mole in vacuum.

Table 4. Relative probabilities of different minimum energy configurations obtained during stacking, in-plane and terminal interactions in vacuum and in benzene. Average dielectric constant of benzene = 2.25.

Configuration	Energy in Vacuum kcal/mole	Energy in Dielectric Med. kcal/mole	Probability (%) at Different Temperatures					
			300 K		399 K*		450 K	
			A	B	A	B	A	B
X (0°) Y (0°)	-4.698	-2.088	9.5	24.1	14.8	24.3	16.9	24.7
X (180°) Y (0°)	-3.932	-1.748	2.6	12.7	5.6	15.8	7.2	16.9
X (0°) Z (0°)	-6.024	-2.677	87.8	60.2	78.8	51.1	74.7	47.7
X (0°)	-2.095	-0.931	0.1	3.2	0.6	5.7	0.9	6.8
Y (0°)	-1.019	-0.453	0.0	1.4	0.2	3.1	0.3	3.9

* Nematic – Isotropic Transition Temperature.

A Probability in Vacuum.

B Probability in Dielectric Medium.

Table 5. Comparative picture of translational rigidities along the X-axis during stacking and in-plane interactions between a pair of **EPPH** molecules in a dielectric medium (benzene).

Temperature (K)	Translational Rigidities	
	Stacking Interactions	In-plane Interactions
300	0.96	0.54
399*	0.83	0.53
450	0.79	0.52

* Nematic – Isotropic Transition Temperature.

Correlation of the Results with the Nematogenicity

The nematic character of a liquid crystal is manifested by its translational freedom along the long molecular axis. Therefore, for stacked and in-plane interactions, changes in probabilities for translations at intervals of 2 Å were reported.

Figure 3 shows the results obtained for stacking interactions. It may be observed that stacking interactions have lesser translational freedom. Table 5 shows the ratio of probability being at the maximum probable point to having ± 2 Å displacement along the long molecular axis during stacking interactions is 0.82 at nematic – isotropic transition temperature. However, at room temperature the value is 0.96 indicating a very strong binding at lower temperature but with the increase of temperature, the molecules obtain sufficiently freedom to slide along the long molecular axis. Such translational freedom is much more pronounced in planar interactions. Thus, even at room temperature this ratio is 0.54, which reduces to 0.52

at the transition temperature. It may be noted that (see Fig. 6) though the freedom is considerable for smaller translation, longer translations are not in general permitted. Thus, small movements of the molecules are only possible in the mesomorphic range.

Further, it is clear from the above discussion that the isolated consideration for any particular degree of freedom manifests, in general, a preference for aligned structure with some allowance of deviation from its minimum energy configuration. Also, each configuration has its own minimum energy structure for every degree of freedom. Thus in a molecular assembly, a number of local minimum energy configuration exists; all of them have their own importance as in case of close molecular packing, any molecule, depending on its own spatial position may be forced to assume a local minimum energy configuration. The global minimum is, however, of paramount importance because while coming down from a very high temperature when the molecules have a complete disordered distribution, the global minimum has the maximum probability of occupancy and the other minima have a sequential preference depending on their individual relative probability.

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