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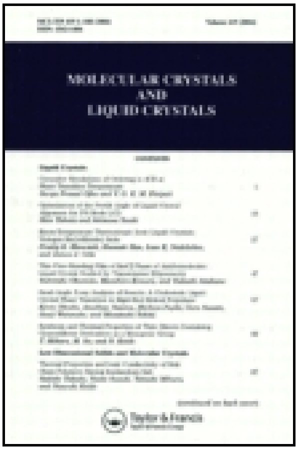

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Origin and Model for Cooperative Host-Guest Interaction Affecting the Orientation of Guests in Oriented Nematic Hosts

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Origin and Model for *Cooperative* Host–Guest Interaction Affecting the Orientation of Guests in Oriented Nematic Hosts

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It has been observed for the binary systems of oriented nematic hosts and nonmesomorphic guests (substituted anthraquinones) that the orientational orders of amino-substituted anthraquinones ascend with increasing guest concentrations. A new quantitative and experimental procedure has been proposed for obtaining the host–guest isotropic *dispersion,* isotropic *electrostatic,* anisotropic *dispersion, and* anisotropic *electrostatic interaction energies. Among these four host–guest interaction energies, the host–guest* isotropic *dispersion interaction energy alone is demonstrated to be well correlated with the concentration dependence of the orientational order of the guest. A model is also proposed for the* cooperative *and* isotropic *host–guest interaction.*

Keywords: Isotropic dispersion force; nematic host–guest cooperative interaction; orientational order

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INTRODUCTION

It has been shown that both the dispersion attractive force [1–6] and the hard-core repulsive force [7–16] play dominant roles in anisotropic intermolecular interaction to induce anisotropic molecular arrangements of the liquid crystals [17–21]. For a binary system of nematic host and nonmesomorphic guest, however, hard-core repulsive forces were shown not to contribute considerably to anisotropic host–guest interaction [22]. Furthermore, *anisotropic* dispersion energy, introduced first in the liquid-crystal theory proposed by Maier and Saupe [1], is estimated to be at least an order of magnitude smaller than that required by their theory, suggesting the importance of the *isotropic* dispersion force [23]. Thus, in the present study, we analyze attractive host–guest interaction to demonstrate the important role of the host–guest *isotropic* dispersion force in the *cooperative* induction of the orientation of guests in oriented nematic hosts. For some binary systems of nematic hosts and nonmesomorphic guests, we have previously investigated the effects of the guest concentrations on the nematic–isotropic transition temperature (T_{ni}) of the host and on the dichroic ratio (R_{d}), a measure of the orientational order, of the guest. We found that T_{ni} and R_{d} are both elevated with increasing guest concentrations in the case of the CPB (4-cyano-4′-pentylbiphenyl; host)–D37 (1,5-di(p-n-butylanilino)anthraquinone; guest) system [24]. This phenomenon has been considered to be induced by an attractive host–guest interaction of the *many-body* and *cooperative* type [24]. In the present article, we study the dependence of T_{ni} and R_{d} on guest concentrations for binary mixtures of nematogenic hosts and nonmesomorphic guests, the guests being several anthraquinones with simple substituents such as amino and/or hydroxy groups. Furthermore, the nature of the attractive host–guest interactions are analyzed by applying the theories of Maier and Saupe [1] and McRae [25] to get an insight into the ideas of *cooperative* and *isotropic* aspects of the host–guest interaction.

EXPERIMENTAL

The samples used are CPB (Merck) and 4-(4′-n-butylcyclohexyl)-cyanocyclohexane (abbreviated to CCH4, Merck) for nematogenic hosts and anthraquinone (AQ), 1-aminoanthraquinone (1-NH_2AQ), 2-aminoanthraquinone (2-NH_2AQ), 1,4-diaminoanthraquinone (1,4-NH_2AQ), 1,5-diaminoanthraquinone (1,5-NH_2AQ), 1,4,5,8-tetraaminoanthraquinone (TAAQ), 1-hydroxyanthraquinone (1-OHAQ), 1,4-dihydroxyanthraquinone (1,4-OHAQ), 1,5-dihydroxyanthraquinone (1,5-OHAQ), 1-amino-4-hydroxyanthraquinone (1-NH_2-4-OHAQ), and 1,5-dichloroanthraquinone (1,5-ClAQ) for nonmesomorphic guests. These guest samples were obtained commercially from Tokyo Kasei Kogyo Co., Ltd., and used without further purification, except for TAAQ (Aldrich), which was recrystallized three times from ethanol because of its low purity (35%).

A sandwich cell was prepared using two borosilicate glass plates coated with PVA (polyvinylalcohol). The coated plates were rubbed to attain a homogeneous alignment of the nematic host. The T_{ni} value of the nematic host was determined by the method previously reported [24]. As quantitative measures of the degrees of changes in T_{ni} and in R_{d} with increasing guest concentration, the $\beta\,(=-\mathrm{d}T_{\mathrm{ni}}{}^{*}/\mathrm{dx})$ [26] and $\beta'(=\mathrm{d}R_{\mathrm{d}}/\mathrm{dx})$ values were evaluated from the slopes of the $T_{\mathrm{ni}}{}^{*}$ vs. x and R_{d} vs. x plots, respectively. $T^{*}_{\mathrm{ni}}\,(=T_{\mathrm{ni}}/T^{0}_{\mathrm{ni}})$ and x are the reduced temperature and the molar fraction of the guest, respectively. Here, T_{ni} and $T_{\mathrm{ni}}{}^{0}$ are the nematic–isotropic transition temperatures with and without guests, respectively. The R_{d} value of the guest in the oriented nematic host is defined as $A_{\parallel}/A_{\perp}$, where $A_{\parallel}$ and $A_{\perp}$ are the absorbances for the light beams polarized parallel to and perpendicular to the rubbing direction, respectively. The R_{d} value was determined at the peak position of the longest wavelength absorption band of the guest, which is polarized along the longer molecular axis. The nematic host exhibited no absorption in this wavelength region. The order parameter (S) of a guest in the oriented nematic host was experimentally evaluated as $S = (A_{\parallel} - A_{\perp})/(A_{\parallel} - 2A_{\perp}) = (R_{\mathrm{d}} - 1)/(R_{\mathrm{d}} + 2)$, giving the longer molecular axis orientational order of the guest. The S value for 2-NH_2AQ was corrected because the transition moment for the longest wavelength absorption band of 2-NH_2AQ deviates from the longer molecular axis to a larger extent [27].

The anisotropic relative permittivity ($\varepsilon_{\perp}$) and the anisotropy in the relative permittivities ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$) for the anisotropic nematic host were determined from the voltage dependence of the capacitance, which is measured for the nematic host oriented homogeneously between the two glass plates. These two glass plates are coated with ITO (indium tin oxide) thin films and further with PVA thin film, followed by rubbing. The anisotropic relative permittivity of $\varepsilon_{\parallel}$ is given as $\varepsilon_{\parallel} = \Delta\varepsilon + \varepsilon_{\perp}$. Here, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are defined as the relative permittivities for the electric field parallel to and perpendicular to the rubbing direction, respectively. The capacitance was measured using an LCR meter YHP4275A (Yokokawa-Hewlett-Packard). The anisotropic refractive index ($n_{\perp}$) for the anisotropic nematic host was determined by measuring the refraction angle of the light (He–Ne laser; $\lambda = 632.8\,\mathrm{nm}$), polarized perpendicular to the rubbing direction, passing through

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the liquid-crystalline cell with a **wedgy-shaped** gap. In addition, the anisotropy in the refractive indices ($\Delta n = n_{\|} - n_{\perp}$) was determined from the voltage dependence of the transmittance for the unpolarized light propagating through crossed nicols, between which the liquid-crystalline cell used for the determination of the anisotropic relative permittivities is sandwiched. The anisotropic refractive index of $n_{\|}$ is given as $n_{\|} = \Delta n + n_{\perp}$. The isotropic relative permittivity ($\varepsilon_{\mathrm{iso}}$) and isotropic refractive index (n_{iso}) for the isotropic host were measured by heating the nematic host above T_{ni}.

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RESULTS AND DISCUSSION

Concentration Dependence of T_{ni} and R_{d}

In Fig. 1, the T_{ni} values were plotted against the guest concentrations for various guests of substituted anthraquinones in the nematic hosts of (a) CPB and (b) CCH4. Similar tendencies were seen in the effects of the guest concentration on T_{ni} of both hosts. That is, both T_{ni} values of CPB and CCH4 ascended with increasing concentrations of the guests of 1,5-NH_2AQ, 1,4-NH_2AQ, 1-NH_2AQ, and 1,5-OHAQ, while they descended for the guests of AQ and 1,5-ClAQ.

Figure 2 shows the $-\beta$ vs. S plots for the guests in the nematic hosts of CPB and CCH4, the β values being evaluated from the slopes of the straight lines in Fig. 1. The S values for all the guests adopted in this figure were determined at constant guest concentrations and at constant temperatures appropriate to the nematic hosts of CPB (20°C) and CCH4 (55°C). It is inferred from Fig. 2 that the order parameters of the guests are well correlated with the $-\beta$ values of the nematic hosts. This implies that the guest exhibiting a higher orientational order in a nematic host has a higher ability to raise T_{ni} or to enhance the thermal stability of the molecular orientation of the host. This correlation suggests that the molecular orientation of the guest induced by the oriented nematic host and the enhancement of the molecular orientational order of the host induced by the guest are both caused by the same kind of host–guest intermolecular force. As described in the introductory section, the attractive intermolecular force responsible for the molecular arrangement of the nematic host is suggested to be the *isotropic* dispersion force rather than the *anisotropic* one [23]. Thus, we investigated to see if there were any correlations between the host–guest *isotropic* (or *anisotropic*) dispersion force and the thermal stability ($-\beta$) of the host (or the longer-molecular-axis orientational order (S) of the guest in the host). The scaled or relative anisotropies in polarizabilities ($\Delta\alpha^* = \Delta\alpha/(\alpha_{\mathrm{i}} + \alpha_{\mathrm{j}} + \alpha_{\mathrm{k}})$) [28,29] and the

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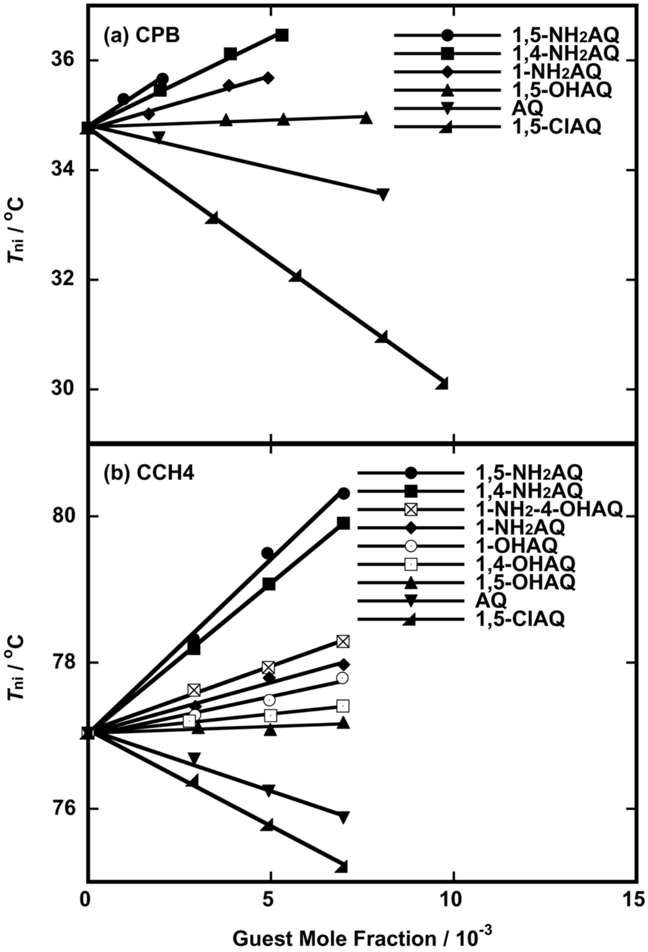

FIGURE 1 Plots of T_{ni} against guest mole fractions for various guests of substituted anthraquinones in nematic hosts of (a) CPB and (b) CCH4.

lowest (first) electronic absorption band energies (ΔE: estimated from the band maximum position) of the guests were used as a measure of the magnitudes for the *anisotropic* and the whole (*isotropic* + *anisotropic*) dispersion forces between a host and various guests, respectively. Here, $\Delta\alpha$(anisotropy in polarizability) $= 2\alpha_{\mathrm{i}} - \alpha_{\mathrm{j}} - \alpha_{\mathrm{k}}$, where *i, j*, and *k* are the axes of the highest, medium, and lowest polarizability, respectively [30]. The values of α_{i}, α_{j}, and α_{k} for substituted AQ were estimated from those for AQ [31] and bond polarizabilities [29,32–34]. The larger the $\Delta\alpha$ value of the guest, the stronger

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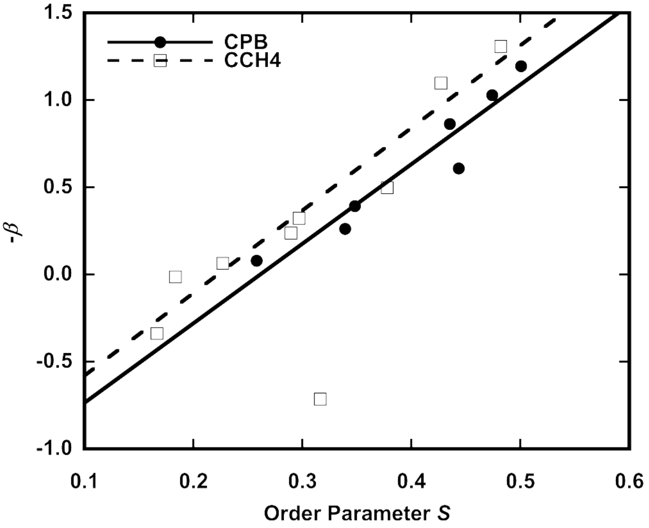

FIGURE 2 $-\beta$ vs. S plots for guests in nematic hosts of CPB (circlar dots with solid straight line) and CCH4 (square dots with dashed straight line).

the host–guest *anisotropic* dispersion force, whereas the smaller the ΔE value of the guest, the stronger the total (*isotropic* + *anisotropic*) host–guest dispersion force. The latter criterion is based on the theory for the *isotropic* and *anisotropic* dispersion energies by Maier and Saupe [1].

The $-\beta$ vs. $\Delta\alpha^*$, S vs. $\Delta\alpha^*$ and $-\beta$ vs. ΔE plots are shown in Fig. 3–5, respectively, for the guests in the nematic hosts of CPB and CCH4. It is found from these figures that there exist roughly linear relationships with negative slopes for the $-\beta$ vs. $\Delta\alpha^*$, S vs. $\Delta\alpha^*$, and $-\beta$ vs. ΔE plots. That is, the guests with larger $\Delta\alpha^*$ values exhibit smaller $-\beta$ or S values, whereas the guests with smaller ΔE values induce larger $-\beta$ values. It is, therefore, demonstrated that the larger the host–guest *anisotropic* dispersion force, the smaller the orientational order of the guest and the rate of increase in T_{ni} of the host, whereas the larger the total (*isotropic* + *anisotropic*) host–guest dispersion force, the larger the orientational order of the guest and the rate of increase in T_{ni} of the host. The combination of these two demonstrations leads to the conclusion that the *isotropic* host–guest dispersion force is considered to play a central role in the latter demonstration. This implies that the larger the host–guest *isotropic* dispersion force, the larger the orientational order of the guest and the increases in T_{ni} of the host. It is therefore shown that the host–guest *anisotropic* and

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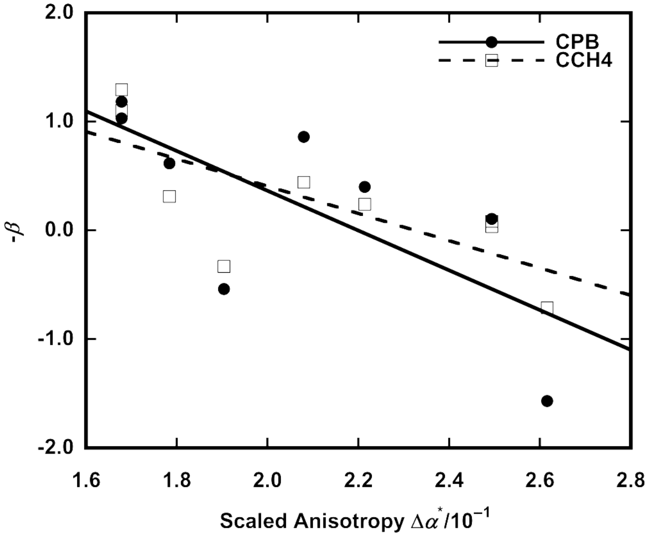

FIGURE 3 $-\beta$ vs. $\Delta\alpha^*$ plots for guests in nematic hosts of CPB (circlar dots with solid straight line) and CCH4 (square dots with dashed straight line).

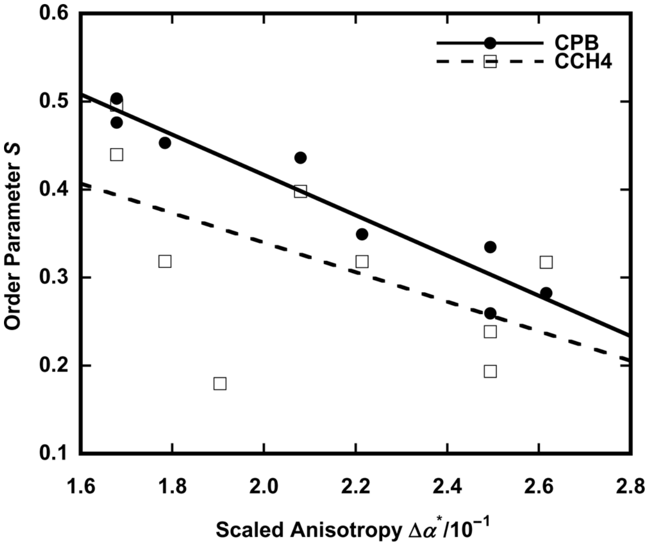

FIGURE 4 S vs. $\Delta\alpha^*$ plots for the guests in the nematic hosts of CPB (circlar dots with solid straight line) and CCH4 (square dots with dashed straight line).

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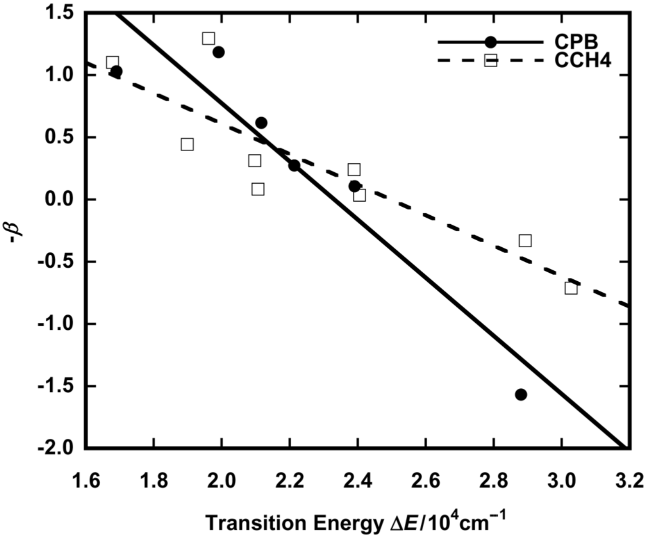

FIGURE 5 $-\beta$ vs. ΔE plots for guests in nematic hosts of CPB (circlar dots with solid straight line) and CCH4 (square dots with dashed straight line).

isotropic dispersion forces exhibit such opposing effects; the *anisotropic* force weakens the orientational order of the guest and the increase of T_{ni} of the host whereas the *isotropic* force strengthens them. Thus, it is shown qualitatively that the dispersion force between host and guest, responsible for the orientation of the guest and for the increases in T_{ni} of the host, is not *anisotropic* but *isotropic*. It was further observed that the R_{d} values of the guests in the oriented nematic hosts ascended with increasing concentrations of the guests (Fig. 6), R_{d} values being observed at constant temperatures appropriate to the nematic hosts of CPB (20°C) and CCH4 (55°C). Here, amino-substituted anthraquinones were selected as guests because they induced marked elevations of T_{ni} with their increasing concentrations (Fig. 1), TAAQ being newly included. The β' values evaluated from the slopes of the straight lines in Fig. 6 are given in parentheses. A few articles have already been published concerning guest-concentration dependence of the orientation of guest in the nematic host [24,35,36].

Origin of the Host–Guest Interaction Affecting R_{d}

To elicit a sounder confirmation of this view and to analyze the concentration dependence of the R_{d} values mentioned previously, the host–guest *isotropic* and *anisotropic* interaction energies were

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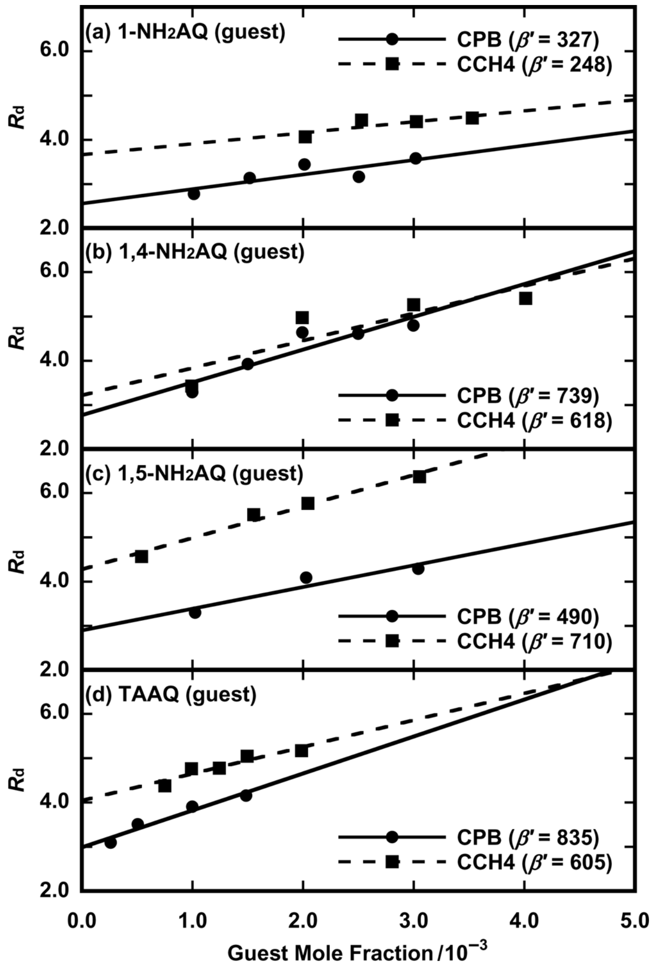

FIGURE 6 R_d vs. guest mole fraction plots for guests of (a) 1-NH_2AQ, (b) 1,4-NH_2AQ, (c) 1,5-NH_2AQ, and (d) TAAQ in nematic hosts of CPB (circle dots with solid straight line) and CCH4 (square dots with dashed straight line). β' values evaluated from slopes of straight lines are given in parentheses.

experimentally estimated. These estimated host–guest interaction energies were further decomposed into the host–guest dispersion (including induction) and electrostatic energies by Eq. (1), which was theoretically derived for the effects of solute–solvent electric dipole interactions on electronic absorption band energies (in wavenumber) in solution spectra by E. G. McRae [25], as follows:

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TABLE 1 Relative Permittivities and Refractive Indices for Isotropic and Anisotropic Hosts of CCH4 and CPB

	Host	
Parameter	CCH4	CPB
$\Delta\varepsilon$[a]	4.066	10.006
$\varepsilon_{\perp}$[a]	3.770	5.504
$\varepsilon_{\parallel}$[a]	7.836	15.51
$\varepsilon_{\mathrm{iso}}$	5.560	9.407
n_{iso}	1.441	1.579
Δn	0.055	0.206
$n_{\perp}$	1.416	1.464
$n_{\parallel}$[c]	1.471	1.670

[a] See the text for the meanings of notations used.
[b] Given as $\varepsilon_{\parallel} = \Delta\varepsilon + \varepsilon_{\perp}$.
[c] Given as $n_{\parallel} = \Delta n + n_{\perp}$.

$$\tilde{\nu} = \tilde{\nu}_{\mathrm{g}} + (\mathrm{A}+\mathrm{B})\left[\frac{n^2-1}{2n^2+1}\right] + \mathrm{C}\left[\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right]. \tag{1}$$

To apply this equation to the present problem, we measured the relative permittivities (ε) and refractive indices (n) of the isotropic and anisotropic hosts and also the first electronic absorption band energies [in wavenumber ($\tilde{\nu}$)] for the guests dissolved in the isotropic and anisotropic hosts. These measured values are given in Tables 1 and 2.

As a first step, the first transition energy ($\tilde{\nu}_{\mathrm{g}}$) of the gaseous guest and unknown constants ($\mathrm{A}_{\mathrm{iso}} + \mathrm{B}_{\mathrm{iso}}$ and $\mathrm{C}_{\mathrm{iso}}$) of the guest in the isotropic host were evaluated by solving simultaneous linear equations in three unknowns. These equations are obtained by substitutions of the n_{iso} and $\varepsilon_{\mathrm{iso}}$ values for the three kinds of isotropic hosts of

TABLE 2 First Electronic Absorption B and Energies $\tilde{\nu}$ for Guests in Isotropic and Anisotropic Hosts

	$\tilde{\nu}_{\mathrm{iso}}$ (cm^{-1}) in isotropic host			$\tilde{\nu}_{\mathrm{aniso}}$ (cm^{-1}) in anisotropic host	
Guest	CCH4	CPB	Ethanol	CCH4	CPB
1-NH_2AQ	21395	21249	20964	21164	20973
1,5-NH_2AQ	20799	20551	20408	19908	19616
1,4-NH_2AQ	17106	16875	16835	16903	16790
TAAQ	15637	15475	15798	15571	15337

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TABLE 3 Decomposition of the Guest–Host *Isotropic* Interaction Energy into Dispersion and Electrostatic Interaction Energies

Guest	Host	*Isotropic* interaction energy[a] (cm^{-1})	*Isotropic* dispersion interaction energy[b] (cm^{-1})	*Isotropic* electrostatic interaction energy[c] (cm^{-1})
1-NH_2AQ	CCH4	−754	−270	−485
	CPB	−900	−322	−578
	Ethanol	−1185	−234	−951
1,5-NH_2AQ	CCH4	−1280	−768	−512
	CPB	−1528	−917	−611
	Ethanol	−1671	−666	−1005
1,4-NH_2AQ	CCH4	−1029	−800	−392
	CPB	−1260	−956	−467
	Ethanol	−1300	−694	−769
TAAQ	CCH4	−835	−881	46
	CPB	−997	−1051	55
	Ethanol	−674	−764	90

[a] $\Delta\tilde{\nu} = \tilde{\nu}_{\mathrm{iso}} - \tilde{\nu}_{\mathrm{g}}$.

[b] $(\mathrm{A}_{\mathrm{iso}} + \mathrm{B}_{\mathrm{iso}})\left[\frac{n_{\mathrm{iso}}^2-1}{2n_{\mathrm{iso}}^2+1}\right]$.

[c] $\mathrm{C}_{\mathrm{iso}}\left[\frac{\varepsilon_{\mathrm{iso}}-1}{\varepsilon_{\mathrm{iso}}+2} - \frac{n_{\mathrm{iso}}^2-1}{n_{\mathrm{iso}}^2+2}\right]$.

CCH4, CPB, and ethanol, and the $\tilde{\nu}_{\mathrm{iso}}$ values for the guest in these isotropic hosts into Eq. (1). Then, the right-side second and third terms in Eq. (1) can be evaluated as given in Table 3 for each guest in the isotropic hosts. The band shift energy $\Delta\tilde{\nu}(=\tilde{\nu}_{\mathrm{iso}} - \tilde{\nu}_{\mathrm{g}})$ is considered to be a measure of the host–guest *isotropic* interaction energy. According to Eq. (1), this *isotropic* interaction energy can be decomposed into the right-side second [the *isotropic* dispersion (including induction) energy] and third (the *isotropic* electrostatic energy) terms as tabulated in Table 3. Similarly, the constants ($\mathrm{A}_{\mathrm{aniso}} + \mathrm{B}_{\mathrm{aniso}}$ and $\mathrm{C}_{\mathrm{aniso}}$) for the guest in the anisotropic liquid-crystalline host were evaluated by solving simultaneous linear equations in two unknowns, which were obtained by substitutions of the $n_{\parallel}$ and $\varepsilon_{\parallel}$ values for the two kinds of liquid-crystalline hosts of CCH4 and CPB and the $\tilde{\nu}_{\mathrm{aniso}}$ values for the guest in these liquid-crystalline hosts along with the $\tilde{\nu}_{\mathrm{g}}$ value into Eq. (1). The $\mathrm{A}_{\mathrm{aniso}} + \mathrm{B}_{\mathrm{aniso}}$ and $\mathrm{C}_{\mathrm{aniso}}$ values thus obtained yield the right-side second and third terms of Eq. (1) for each guest in the anisotropic liquid-crystalline host as shown in Table 4. In this table, the band shift energy $\Delta\tilde{\nu}(=\tilde{\nu}_{\mathrm{aniso}} - \tilde{\nu}_{\mathrm{g}})$ is considered to be a measure of the host–guest *isotropic* + *anisotropic* interaction energy.

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TABLE 4 Decomposition of the Guest–Host *Isotropic* + *Anisotropic* Interaction Energy into Dispersion and Electrostatic Interaction Energies

Guest	Host	*Isotropic* + *anisotropic* interaction energy[a] (cm^{-1})	*Isotropic* + *anisotropic* dispersion interaction energy[b] (cm^{-1})	*Isotropic* + anisotropic electrostatic interaction energy[c] (cm^{-1})
1-NH_2AQ	CCH4	−985	−649	−336
	CPB	−1176	−808	−368
1,5-NH_2AQ	CCH4	−2171	−568	−1603
	CPB	−2463	−707	−1756
1,4-NH_2AQ	CCH4	−1232	30	−1262
	CPB	−1345	38	−1383
TAAQ	CCH4	−901	−990	89
	CPB	−1135	−1232	98

[a] $\Delta\tilde{\nu} = \tilde{\nu}_{\mathrm{aniso}} - \tilde{\nu}_{\mathrm{g}}$.

[b] $(\mathrm{A}_{\mathrm{aniso}} + \mathrm{B}_{\mathrm{aniso}})\left[\frac{n_{\parallel}^2 - 1}{2n_{\parallel}^2 + 1}\right]$.

[c] $\mathrm{C}_{\mathrm{aniso}}\left[\frac{\varepsilon_{\parallel} - 1}{\varepsilon_{\parallel} + 2} - \frac{n_{\parallel}^2 - 1}{n_{\parallel}^2 + 2}\right]$.

Subtraction of the host–guest interaction energies in Table 3 from the corresponding ones in Table 4 gives the results in Table 5, which show the decomposition of the host–guest *anisotropic* interaction energy into dispersion and electrostatic energies. It is interesting to note that the *anisotropic* host–guest dispersion and electrostatic forces are respectively attractive and repulsive for both TAAQ and 1-NH_2AQ but repulsive and attractive for both 1,4-NH_2AQ and 1,5-NH_2AQ (Table 5). Tables 3 and 5 reveal that the host–guest dispersion and electrostatic forces, which contribute to the host–guest *isotropic* and *anisotropic* intermolecular interactions, are controlled by the guests, irrespective of the hosts. That is, both the *isotropic* and *anisotropic* interactions are mainly contributed by the dispersion force for TAAQ; the *isotropic* and *anisotropic* ones mainly by the electrostatic and dispersion forces, respectively, for 1-NH_2AQ; and the *isotropic* one by both the electrostatic and dispersion forces to the same degree and the *anisotropic* one mainly by the electrostatic force for 1,4-NH_2AQ and 1,5-NH_2AQ. These results may be specific to the present host–guest system and are considered to arise from the difference in the polarity natures of guests due to different number of amino groups. It may be due to the presence of the polar cyano group on both hosts of CPB and CCH4 that the nature of the host–guest interaction force was rather insensitive to the natures of hosts.

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TABLE 5 Decomposition of the Guest–Host *Anisotropic* Interaction Energy into Dispersion and Electrostatic Interaction Energies

Guest	Host	*Anisotropic* interaction energy[a] (cm^{-1})	*Anisotropic* dispersion interaction energy[b] (cm^{-1})	*Anisotropic* electrostatic interaction energy[c] (cm^{-1})
1-$\mathrm{NH_2}$AQ	CCH4	−231	−379	149
	CPB	−276	−486	210
1,5-$\mathrm{NH_2}$AQ	CCH4	−891	200	−1091
	CPB	−935	210	−1145
1,4-$\mathrm{NH_2}$AQ	CCH4	−203	830	−870
	CPB	−85	994	−916
TAAQ	CCH4	−66	−109	43
	CPB	−138	−181	43

[a] $\Delta\tilde{\nu} = \tilde{\nu}_{\mathrm{aniso}} - \tilde{\nu}_{\mathrm{iso}}$.

[b] $(\mathrm{A}_{\mathrm{aniso}} + \mathrm{B}_{\mathrm{aniso}})\left[\frac{n_{\parallel}^2-1}{2n_{\parallel}^2+1}\right] - (\mathrm{A}_{\mathrm{iso}} + \mathrm{B}_{\mathrm{iso}})\left[\frac{n_{\mathrm{iso}}^2-1}{2n_{\mathrm{iso}}^2+1}\right]$.

[c] $\mathrm{C}_{\mathrm{aniso}}\left[\frac{\varepsilon_{\parallel}-1}{\varepsilon_{\parallel}+2} - \frac{n_{\parallel}^2-1}{n_{\parallel}^2+2}\right] - \mathrm{C}_{\mathrm{iso}}\left[\frac{\varepsilon_{\mathrm{iso}}-1}{\varepsilon_{\mathrm{iso}}+2} - \frac{n_{\mathrm{iso}}^2-1}{n_{\mathrm{iso}}^2+2}\right]$.

The β' vs. host–guest interaction energy plots show (1) a good linear relationship with negative slope concerning isotropic dispersion energy for the guests in both hosts of CPB and CCH4 (Fig. 7a); (2) a roughly linear relationship with positive slope and no relationship concerning isotropic electrostatic energy for the guests in CPB and CCH4, respectively (Fig. 7b); (3) a roughly linear relationship with positive slope concerning anisotropic dispersion energy for the guests in both hosts of CPB and CCH4 (Fig. 7c); and (4) no relationship and a roughly linear relationship with negative slope concerning anisotropic electrostatic energy for the guests in CPB and CCH4, respectively (Fig. 7d). The rise in R_{d} with an increase in guest concentrations is, therefore, quantitatively demonstrated to be induced mainly by the attractive host–guest isotropic dispersion force and partly by the repulsive host–guest anisotropic dispersion force for the guest in both hosts of CPB and CCH4; it is also demonstrated to be further partly induced by the attractive host–guest anisotropic electrostatic force for the guests in CCH4 and to be partly hindered by the attractive host–guest isotropic electrostatic force for the guests in CPB.

Model for the Host–Guest Interaction Affecting R_{d}

A single guest molecule is more or less perturbing host–host interactions, which induce the orientations of nematic host molecules. The

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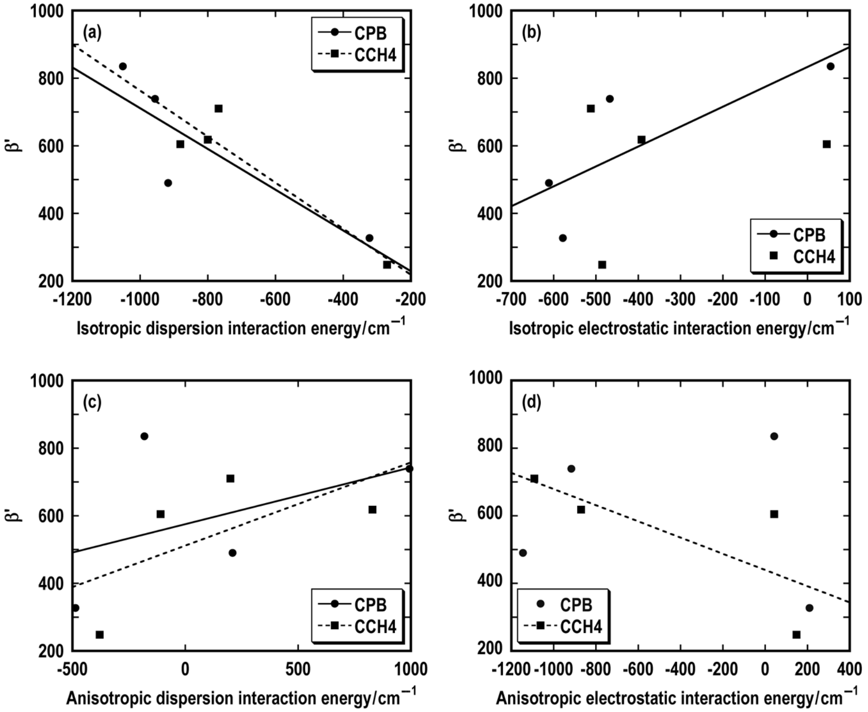

FIGURE 7 Plots of β' against guest–host interaction energies for guests in nematic hosts of CPB (circlar dots with solid straight line) and CCH4 (square dots with dashed straight line).

total addition of the perturbations by all guest molecules gives the total perturbation for the whole molecular orientational order of the nematic host, which induces the change in the thermal stability (T_{ni}) of the host. Because the total perturbations by the guest molecules increase with increasing the number of guest molecules, T_{ni} is simply considered to be dependent on the guest concentrations. When the host–guest interaction is attractive (repulsive), the perturbation by the guest molecule will enforce (disturb) the ordered molecular orientation of the nematic host and T_{ni} will be elevated (lowered) with increasing guest concentrations. However, it is considered that the number of guest molecules is much smaller than that of host molecules, as is the case in the present experiment, direct interaction between guest molecules is impossible, and a single guest molecule interacts with several nearby host molecules directly. Moreover, the orientation of a single guest molecule in the oriented nematic host is

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normally controlled only by the whole nature of these interactions of this guest molecule with the several neighboring host molecules. Thus, the orientations of all guest molecules are simply maintained by the total pairwise addition of the host–guest interactions summed up for all guest molecules. Therefore, the orientational order (or R_d) of the guest in the oriented nematic host is simply considered to be constant irrespective of the number of guest molecules and to be independent of the guest concentrations.

The dependence of R_d on guest concentrations was analyzed based on a model for the *cooperative* and *isotropic* host–guest interaction illustrated in Fig. 8. The important concept for the *cooperative* and *isotropic* host–guest interaction model in Fig. 8 is that the *anisotropic* host–guest interaction induces the original orientation of the guest molecule in the oriented nematic host, and this original orientation is *indirectly* and *cooperatively* influenced by the *isotropic* host–guest interaction. As illustrated in Fig. 8, the primary host–guest interaction is considered to propagate through host molecules by perturbing the host–host interaction sequentially and reaches another guest molecule to generate the secondary host–guest interaction. This secondary

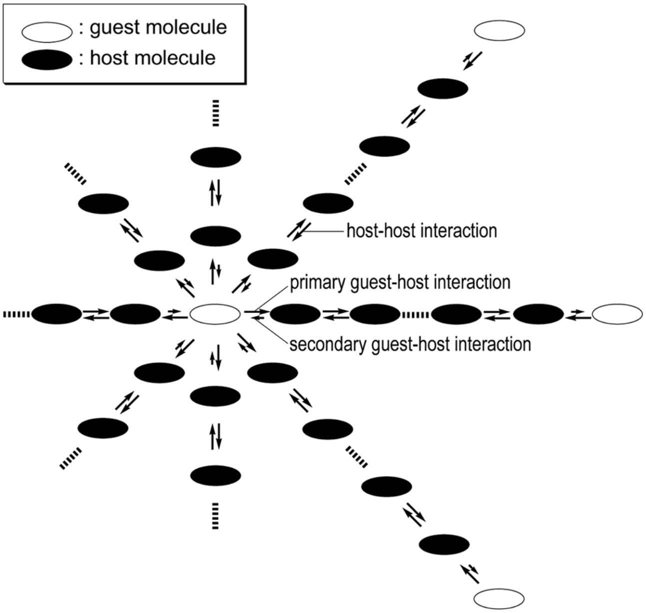

FIGURE 8 Model for *cooperative* and *isotropic* guest–host interaction.

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host–guest interaction is encountered only when the primary host–guest interaction is large enough to reach another guest molecule (case 1). When the primary host–guest interaction is small (case 2), this is not the case.

In case 1, the host–guest interaction acquires a character of *nonpairwise additivity* due to the emergence of *cooperative* action of the primary and secondary host–guest interactions. This leads to the conclusion that the host–guest interaction is under the influence of other guest molecules. That is, the orientation of a guest molecule in the oriented nematic host, which might be originally induced by the *anisotropic* host–guest attractive or repulsive interaction, is *indirectly* and *cooperatively* influenced by other guest molecules and is dependent on the guest concentrations. This concentration dependence arises from two situations in the model of Fig. 8. First, the number of outer guest molecules, which are neighbors to the central guest molecule, becomes larger with an increase in the guest concentration, resulting in generation of more secondary host–guest interactions for the central guest molecule. Second, the distance between the central and outer quest molecules becomes shorter, that is, the number of the host molecules intersecting the central and outer guest molecules becomes smaller with an increase in the guest concentration, resulting in a generation of stronger secondary host–guest interactions for the central guest molecule. When the host–guest interaction is attractive, it can enforce the original orientation of the central guest molecule via the *cooperative* action of the primary and secondary host–guest interactions. Furthermore, when the host–guest interactions are *isotropic*, they can propagate in all directions and would be more effective in allowing themselves to be originated from more outer guest molecules to reach the central guest molecule as secondary ones than they would be when *anisotropic*. Thus, the *isotropic* host–guest attractive interaction induces a more effective *cooperative* action of the primary and secondary host–guest interactions and would have, coupled with the *anisotropic* host–guest interaction, a higher ability to elevate R_d with increasing guest concentration than the *anisotropic* host–guest interaction alone. That is, it is proposed in the host–guest interaction model in Fig. 8 that the *isotropic* host–guest interaction is coupled with the *anisotropic* one, and this coupling can, even if the *anisotropic* host–guest interaction is relatively weak as is the case in our host–guest interaction (see Tables 3 and 4), give rise to a strong anisotropic character in the host–guest interaction, which induces in turn an effective orientation of guest in oriented nematic host. If this is the case, it is not curious that the main host–guest dispersion force responsible for the orientation of guest in oriented nematic host has been qualitatively shown to be not *anisotropic* but *isotropic*. Furthermore, in case 1, a single guest molecule shows strong perturbations for the host–host interactions, and the total addition of these perturbations by all guest molecules becomes large enough to show a remarkable dependence of the thermal stability (T_{ni}) of the nematic host on the guest concentration. On the other hand, in case 2, while T_{ni} of the nematic host is weakly dependent on the guest concentrations, R_{d} of the guest is not dependent on the guest concentrations because there is no emergence of *cooperative* action of the primary and secondary host–guest interactions.

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CONCLUSION

The host–guest *isotropic* interaction energies have been defined as the host–guest interaction energies for the guests in the isotropic phase of a nematic host heated above T_{ni}. The dispersion energies in these host–guest *isotropic* interactions have been demonstrated to be in a linear correlation with the β' values. It is therefore suggested that the host–guest interaction character of the guest in the isotropic phase of the nematic host controls the orientation character of the guest in the oriented nematic host in an *indirect* way. The present *cooperative* and *isotropic* host–guest interaction model provides an explanation for why the *isotropic* + *anisotropic* host–guest interaction is more effective for the *indirect* and *cooperative* induction of the concentration-dependent orientation of the guest in the oriented nematic host than the *anisotropic* one itself.

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