J. Phys. Chem. A **2001,** *105,* 6711−6716

Molecular Structures of Related Compounds of Mesogens Studied by ^{1}H NMR Using a Liquid Crystal Solvent: Tolan and *trans*-Azobenzene

Kaori Inoue, Hiroshi Takeuchi, and Shigehiro Konaka*

Division of Chemistry, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

Received: December 31, 2000; In Final Form: April 2, 2001

Molecular structures of tolan and *trans*-azobenzene dissolved in nematic liquid-crystal ZLI 1132 have been determined by proton NMR with the aid of theoretical calculations. They are models of the cores of liquid-crystal molecules of the $RC_6H_4XC_6H_4R'$ type, where R and R′ denote flexible groups and X is the linking unit. Spectral analysis is quite difficult for such a molecule with 10 protons as $C_6H_5XC_6H_5$. In the present study, therefore, the initial spectral parameters that allow spectral assignment have been obtained by analyzing integral curves by means of a genetic algorithm. Structural analyses show that both compounds take planar molecular structures in ZLI 1132. The determined rotational barriers at the dihedral angle of phenyl rings, 90°, in the liquid crystal are larger than those in the gas phase for tolan and *trans*-azobenzene as in the cases of phenyl benzoate and biphenyl. It is reasonable to consider that the liquid-crystal solvent stabilizes the planar or nearly planar structures of solutes.

Introduction

Recently we have determined the gas-phase structures of PAA (*p*-azoxyanisole)[1] and MBBA (4-methoxybenzylidene-4′-*n*-butylaniline),[2] by electron diffraction. They are mesogens of the type $RC_6H_4XC_6H_4R'$, where R and R′ denote flexible groups and X is the linking unit. It has been found that the structures of the molecular cores $C_6H_4XC_6H_4$ are very close to those of the model compounds of the cores, *trans*-azoxybenzene (X = N=N(O)) and *N*-benzylideneaniline (X = CH=N). This result suggests that we can use the model compounds of the core to study the structure of the core of the liquid-crystal molecule.

Tolan, *trans*-azobenzene (see Figure 1), *trans*-azoxybenzene, phenyl benzoate, and several other compounds are also model compounds of the cores of mesogens with two aromatic rings. It is known that the clearing point (the transition temperature between nematic and liquid phases of the liquid crystal) depends on X.[3] The clearing point has empirically been expressed as the sum of the contributions from terminal groups and cores. It has been found on the basis of crystal data that the contribution from the core is related to its length,[4] planarity, and polarity[5] with some exceptions.

Recently the gas-phase structures of *trans*-azobenzene,[6a,b] *trans*-azoxybenzene,[7] and phenyl benzoate,[6a,c] have been determined by electron diffraction by our research group and an apparent relationship has been found between the structure and the contribution of the core to the clearing point.[6] The correlation between the structures and the clearing points suggests that the gas-phase structures of the model compounds of cores are not much different from the structures of the cores of liquid-crystal molecules. The structure of the model compound dissolved in a liquid crystal is expected to be close to that of the core of a mesogenic molecule compared with the gas-phase structure.

However, no structural data in liquid crystals are available for the model compounds of cores except biphenyl[8,9] and phenyl benzoate.[10] The principal purpose of the present study is to determine the structures of tolan and *trans*-azobenzene by ^{1}H NMR using ZLI 1132 as a liquid-crystal solvent. Complex spectra of ten spin systems have been analyzed by using a newly developed technique[11] in which NMR spectra are transformed to integral curves and spectral parameters are refined by means of a genetic algorithm. Experimental structures in the gas phase have been reported for tolan[12,13] and *trans*-azobenzene.[6] In the present study, therefore, the structures in a liquid-crystal solvent are compared with those in the gas phase for tolan and *trans*-azobenzene.

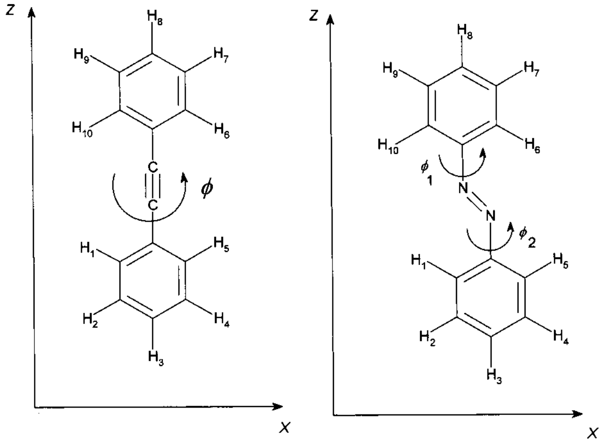

Figure 1. Molecular models of tolan and *trans*-azobenzene. Atom numbering and molecular fixed coordinate axes are shown.

It is noted that tolan and *trans*-azobenzene are interesting from the viewpoint of application. The liquid crystals consisting of molecules with the core of tolan type have low viscosity and are expected to be useful as displays having quick responsiveness. The cis−trans isomerization of azobenzene occurs reversely by UV irradiation and, hence, UV irradiation causes reorientation of liquid-crystal molecules with the core of azobenzene type. This method is noted as a new technique in the liquid-crystal display.[14]

---

* Corresponding author. Fax: +81-11-706-4924. E-mail: konaka@sci.hokudai.ac.jp.

10.1021/jp0045944 CCC: \$20.00

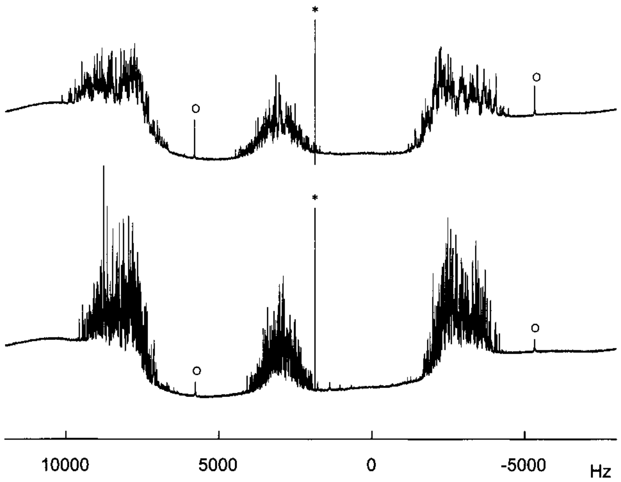

Figure 2. ^{1}H NMR spectra of tolan (bottom) and *trans*-azobenzene (top) dissolved in ZLI 1132. Marks * and o denote signals due to HDO included in D_2O for external lock and water in the sample solution, respectively.

TABLE 1: Coupling Constants and Chemical Shifts of Tolan (in Hz)

$i\ j$	J_{ij}[a]	D_{ij}[b]	D_{ij}^{obs}[a,c]	D_{ij}^{α}[c]	$D_{ij}^{\alpha\ \mathrm{calc}}$
1 2	7.77(6)	−3614.4	−3603.8(1)	−3853.3	−3853.3
1 3	1.25(4)	−465.7	−460.4(3)	−488.7	−488.4
1 4	0.62(5)	−8.2	2.2(1)	3.8	3.6
1 5	1.76(4)	213.3	236.3(5)	246.7	247.0
2 3	7.55(4)	−75.8	29.6(2)	25.9	26.0
2 4	1.51(7)	213.3	235.8(4)	246.2	246.1
1 6		−368.4	−321.9(3)	−315.7	−315.7
1 7		−117.7	−117.2(1)	−116.7	−116.7
1 8		−85.1	−89.1(2)	−89.2	−89.3
2 7		−53.2	−55.2(3)	−55.0	−54.9
2 8		−41.3	−43.8(2)	−43.8	−43.5
3 8		−33.2	−35.1(1)	−35.2	−35.1
$\nu 1-\nu 3$	83.11(8)	−189.6	−233.8(4)		
$\nu 2-\nu 3$	6.58(8)	−373.5	−374.8(5)		
RMS error[d]	0.05		0.45		0.13

[a] The values in parentheses are 3σ. [b] Results of automatic analysis using a genetic algorithm. [c] $D_{ij}^{\alpha} = D_{ij}^{\mathrm{obs}} - \Delta D_{ij}$, where ΔD_{ij} is a vibrational correction. [d] Standard deviations in least-squares calculations on frequencies in the second and fourth columns. Standard deviations in least-squares fitting of D_{ij}^{calc} to D_{ij}^{obs} are listed in the last column.

TABLE 2: Coupling Constants and Chemical Shifts of *trans*-Azobenzene (in Hz)

$i\ j$	J_{ij}[a]	D_{ij}[b]	D_{ij}^{obs}[a,c]	D_{ij}^{α}[c]	$D_{ij}^{\alpha\ \mathrm{calc}}$
1 2	8.03(4)	−3536.6	−3564.2(1)	−3724.1	−3724.1
1 3	1.21(3)	−461.2	−470.6(5)	−490.2	−489.5
1 4	0.46(5)	−14.9	−10.7(1)	−10.8	−11.2
1 5	1.47(6)	193.8	216.6(5)	220.8	221.4
2 3	7.40(3)	−113.2	−52.2(4)	−69.5	−69.1
2 4	1.99(5)	192.8	214.7(5)	218.8	218.8
1 6		−437.9	−483.9(3)	−482.8	−482.6
1 7		−137.7	−151.7(1)	−151.7	−152.3
1 8		−98.0	−111.2(3)	−111.7	−110.5
2 7		−59.8	−67.2(3)	−67.1	−66.1
2 8		−45.8	−51.8(3)	−51.8	−51.2
3 8		−36.2	−41.3(1)	−41.4	−40.8
$\nu 1-\nu 3$	182.03(7)	−153.6	−207.8(5)		
$\nu 2-\nu 3$	18.46(6)	−305.7	−386.4(5)		
RMS error[d]	0.04		0.52		0.54

[a] The values in parentheses are 3σ. [b] Results of automatic analysis using genetic algorithm. [c] $D_{ij}^{\alpha} = D_{ij}^{\mathrm{obs}} - \Delta D_{ij}$, where ΔD_{ij} is a vibrational correction. [d] Standard deviations in least-squares calculations on frequencies in the second and fourth columns. Standard deviations in least-squares fitting of D_{ij}^{calc} to D_{ij}^{obs} are listed in the last column.

Experimental Section

The samples of tolan (Tokyo Chem. Co. Ltd.) and *trans*-azobenzene (Merck) with purity of more than 98% were used without further purification. Each sample was dissolved in ZLI 1132 (Merck) at the concentration of 10 wt %. ^{1}H NMR spectra were measured at 300 K using a JNM EX-400 spectrometer. D_2O was used to lock the magnetic field. Each spectrum is composed of three clusters as shown in Figure 2. The half-height line width of absorption lines is about 3 and 6 Hz in the central part for tolan and *trans*-azobenzene, respectively, whereas it is about 5 and 12 Hz at the ends of the wings of spectra for tolan and *trans*-azobenzene, respectively. ^{1}H NMR spectra of 0.2 M $CDCl_3$ solution were measured to obtain indirect coupling constants.

Theoretical Calculations

To aid structural data analysis, the molecular geometry of tolan was optimized by RHF, MP2, and BP86 calculations using the basis set of 6-31G** and program GAUSSIAN 94.[15] The symmetry of the phenyl group was assumed to be C_{2v}. The C_2 symmetry axis was assumed to coincide with the molecular axis. Geometrical parameters were optimized and energies were calculated by fixing the dihedral angle between two phenyl rings at 0°, 30°, 60°, and 90° in order to search a nonplanar form reported in ref 13. The resultant equilibrium structure was planar in each calculation.[16]

Because the force constants given by BP86/6-31G** calculations are known to reproduce well observed vibrational wavenumbers,[17] the force constants in the equilibrium structure were obtained from the BP86/6-31G** calculations. The force constants of *trans*-azobenzene were cited from ref 6.

Analyses

Spectral Analysis. The indirect coupling constants of tolan and *trans*-azobenzene obtained from ^{1}H NMR spectra of $CDCl_3$ solutions are listed in Tables 1 and 2. They were assumed to be the same as in ZLI 1132.

In general, the molecules with 10 protons in liquid crystals give complicated spectra. This is the case for spectra of tolan and *trans*-azobenzene in ZLI 1132 (see Figure 2). Only the spectra of biphenyl[8,9] and phenyl benzoate[10] have so far been analyzed among the model compounds of the cores. In these pioneering studies, the spectral parameters that allow spectral assignment were obtained by simplifying spectra by partial deuterization[8,10] or by multiple-quantum spectroscopy.[9,18] In the present study, however, we took a different approach developed by us.[11] That is, spectra were integrated and the integral curve was analyzed by using a genetic algorithm[19] to estimate spectral parameters. The merit of using the integral curve is as follows. In the case of spectra, there appear a lot of local minima on the R-value[20] surface. A local minimum is found in the case where some theoretical lines coincide with experimental lines. In integral curves, however, no narrow lines exist, reducing the number of local minima.

Least-squares calculations often need good estimation of initial parameters. This is difficult for tolan and *trans*-azobenzene because spectra are very complex. Therefore, we used a genetic algorithm[19] to estimate the parameters.

In the analysis, the structures of the solutes were taken from the molecular structures determined by gas electron diffraction.[6,13] Order parameters and chemical shifts were refined in the following ranges. For tolan: $0.08 < S_{XX}-S_{YY} < 0.28$, 0.37

$< S_{ZZ} <$ 0.57, 2300 Hz $< \nu_1 <$ 3300 Hz, 2000 Hz $< \nu_2 <$ 3000 Hz, 2400 Hz $< \nu_3 <$ 3400 Hz. For *trans*-azobenzene: 0.11 $< S_{XX}-S_{YY} <$ 0.31, 0.33 $< S_{ZZ} <$ 0.53, 2100 Hz $< \nu_1 <$ 3100 Hz, 2400 Hz $< \nu_2 <$ 3400 Hz, 2600 Hz $< \nu_3 <$ 3600 Hz. The resulting spectral parameters were good enough for assigning spectra and allowing least-squares calculations on absorption frequencies. Final values of chemical shifts and dipolar coupling constants are listed in Tables 1 and 2.

Structural Analysis. Dipolar coupling constants are the quantities averaged over small-amplitude vibrations and internal rotations and they can be written as

$$D_{\mathrm{ij}} = \int P(\{\phi\}) < D_{\mathrm{ij}}(\{\phi\}) >_{\mathrm{vib}} \mathrm{d}\{\phi\} \tag{1}$$

where $\{\phi\}$ denotes ϕ for tolan and ϕ_1 and ϕ_2 for *trans*-azobenzene and $< >_{\mathrm{vib}}$ is the average over small-amplitude vibrations. The statistical weight $P(\{\phi\})$ is given by

$$P(\{\phi\}) = N \exp\{-V(\{\phi\})/k_{\mathrm{B}}T\} \int \exp\{-U(\{\phi\},\Omega)/k_{\mathrm{B}}T\}\mathrm{d}\Omega \tag{2}$$

where $V(\{\phi\})$ and $U(\{\phi\},\Omega)$ denote the potential energy for internal rotation and orienting potential energy, respectively, Ω is the molecular orientation, and N is the normalization factor of $P(\{\phi\})$. This is not exact for *trans*-azobenzene because the kinetic energy includes a coupling term, $(\mathrm{d}\phi_1/\mathrm{d}t)\cdot(\mathrm{d}\phi_2/\mathrm{d}t)$.[21] Recently, however, it has been shown by a very lengthy calculation that eq 2 gives nearly the same results as quantum mechanical calculations at room temperature.[22]

To obtain the dipolar coupling constants $D_{\mathrm{ij}}{}^{\alpha}$ in the r_{α} structure, vibrational corrections, ΔD_{ij} $(= D_{\mathrm{ij}} - D_{\mathrm{ij}}{}^{\alpha})$, were calculated as

$$\Delta D_{\mathrm{ij}} = \int P(\{\phi\})\Delta D_{\mathrm{ij}}(\{\phi\})\mathrm{d}\{\phi\} \tag{3}$$

The force constants given in ref 6 were used for *trans*-azobenzene. The force constants given by BP86/6-31G** calculations were used for tolan after they were scaled so as to reproduce observed vibrational wavenumbers.[17] Resulting force constants and vibrational wavenumbers are given as supplementary information. The calculation of vibrational corrections was repeated until it became consistent with the final molecular structure. The $D_{\mathrm{ij}}{}^{\alpha}$ values thus obtained are listed in Tables 1 and 2 for tolan and *trans*-azobenzene, respectively.

The interproton distances of phenyl groups were determined from $D_{\mathrm{ij}}{}^{\alpha}$ and are listed in Table 3 for tolan and *trans*-azobenzene. In conformational analysis, the potential function was assumed to be

$$V(\phi_{\mathrm{i}}) = (V_2/2)(1 - \cos 2\phi_{\mathrm{i}}) + (V_4/2)(1 - \cos 4\phi_{\mathrm{i}}) \tag{4}$$

where $\phi_{\mathrm{i}} = \phi$ for tolan. In the case of *trans*-azobenzene, the potential function was assumed to be

$$V(\phi_1,\phi_2) = V(\phi_1) + V(\phi_2) \tag{5}$$

Coefficients V_2 and V_4 were determined by least-squares calculations on the D_{ij} values corrected for molecular vibrations. As discussed by Niederberger et al.,[23] D_{16}, D_{17}, and D_{27} are sensitive to $\{\phi\}$ and thus to potential coefficients, V_2 and V_4, whereas D_{18}, D_{28}, and D_{38} are insensitive to $\{\phi\}$. This indicates that V_2 and V_4 are determined mainly from the dipolar coupling constants, D_{16}, D_{17}, and D_{27}.[24]

TABLE 3: Interproton Distance Ratios and Order Parameters of the Phenyl Groups of Tolan and *trans*-Azobenzene

Tolan

	NMR[a]	GED[b]	X-ray[b]	X-ray[c]
$r(1,2)/r(1,5)$	0.574(2)	0.577	0.574	0.576
$r(1,3)/r(1,5)$	0.996(3)	0.997	0.996	0.997
$r(1,4)/r(1,5)$	1.154(3)	1.157	1.152	1.150
$r(2,3)/r(1,5)$	0.577(3)	0.578	0.575	0.572
$r(2,4)/r(1,5)$	1.001(6)	1.005	0.996	0.990
S_{ZZ}[d]	0.476(4)			
$S_{XX}-S_{YY}$[d]	0.153(4)			

trans-Azobenzene

	NMR[a]	GED[e]	X-ray(A)[f]	X-ray(B)[f]
$r(1,2)/r(1,5)$	0.581(3)	0.576	0.575	0.575
$r(1,3)/r(1,5)$	1.002(6)	0.998	1.000	1.001
$r(1,4)/r(1,5)$	1.158(5)	1.155	1.153	1.150
$r(2,3)/r(1,5)$	0.578(7)	0.577	0.577	0.575
$r(2,4)/r(1,5)$	1.004(12)	1.002	0.998	0.991
S_{ZZ}[g]	0.475(9)			
$S_{XX}-S_{YY}$[g]	0.186(9)			

[a] The present work. The values in parentheses are 3σ. [b] Cited from ref 13. [c] Cited from ref 26a. [d] Determined by assuming $r(1,5)$ to be 4.280 Å. [e] Cited from ref 6. [f] Cited from ref 27a. The data in (A) and (B) correspond to different crystal sites. [g] Obtained by assuming $r(1,5)$ to be 4.281 Å (ref 6).

The order parameters of pseudoconformers were calculated as

$$S_{\alpha\beta}(\{\phi\}) = N_{\mathrm{S}} \int (3\cos\theta_{\alpha}\cos\theta_{\beta} - \delta_{\alpha\beta}) \exp\{-U(\{\phi\},\Omega)/k_{\mathrm{B}}T\}\ \mathrm{d}\Omega/2 \tag{6}$$

where N_{S} is the normalization constant of the Boltzmann distribution function and θ_{α} denotes the angle between director and the α-axis of molecular fixed-coordinate system. The orienting potential energy can be expressed in terms of interaction tensor elements $A_{\alpha\beta}(\{\phi\})$ as

$$U(\{\phi\},\Omega) = -\Sigma_{\alpha,\beta}\, A_{\alpha\beta}(\{\phi\})(3\cos\theta_{\alpha}\cos\theta_{\beta} - \delta_{\alpha\beta})/2 \tag{7}$$

It was assumed that the interaction tensor is given by[8,10,25]

$$\mathbf{A}(\{\phi\}) = \Sigma_n\, \mathbf{A}_n(\{\phi\}) \tag{8}$$

where

$$\mathbf{A}_n(\{\phi\}) = \mathbf{T}\mathbf{A}_n\, {}^{t}\mathbf{T} \tag{9}$$

Here, $\mathbf{A}_n(\{\phi\})$ and $\mathbf{A}_n$ are the interaction tensors of the nth segment in the molecular-fixed and local coordinates, respectively, and $\mathbf{T}$ is a transformation matrix. In the present study, the anisotropy, ΔA, and asymmetry, η, of the interaction tensor[25] of the phenyl group were taken as adjustable parameters. In the case of *trans*-azobenzene, the anisotropy of the interaction tensor of the $-\mathrm{N{=}N}-$ segment, ΔA_{NN}, was also adjusted, but η_{NN} was assumed to be zero.

Results and Discussion

Ring Structures and Interaction Parameters. Table 3 shows the interproton distance ratios of the phenyl groups of tolan and *trans*-azobenzene calculated from results of gas electron diffraction (GED)[6b,13] and X-ray diffraction.[13,26a,27a] The ratios of interproton distances of tolan and *trans*-azobenzene observed in ZLI 1132 agree with those in the gas phase[6b,13] and in the solid phase[13,26a,27a] within 1.3%, which is smaller

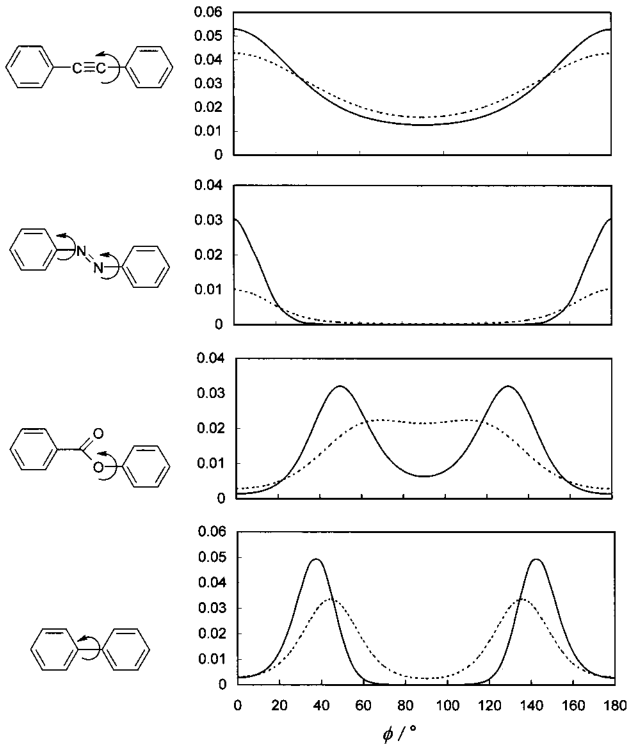

Figure 3. Probability distribution functions $P(\phi)$: results in liquid crystals obtained by NMR (−) and those in the gas phase obtained by electron diffraction (...). In the case of *trans*-azobenzene, a cross section of the probability distribution function, $P(\phi_1,0)$, is shown.

than experimental errors. Thus the structures of the phenyl groups of tolan and *trans*-azobenzene in ZLI 1132 are not significantly different from those in the gas phase and in the crystal.

The values of ΔA, η and ΔA_{NN} are listed in Table 4. It is noted that the interaction parameters, ΔA and η, of the phenyl group of tolan measured at 10 wt % and 300 K are in good agreement with those of *trans*-azobenzene.

Conformation of Tolan. The conformation of tolan is planar according to laser jet spectroscopy[12] and X-ray diffraction.[26] However, a possibility of the existence of nonplanar conformers along with planar ones has been reported by Abramenkov et al. in their GED study.[13] Thus, the conformation of tolan has not been determined unambiguously.

TABLE 4: Coefficients of the Potential Functions for Internal Rotation and Interaction Parameters of Tolan and *trans*-Azobenzene[a]

Tolan

	NMR(V_2)	NMR(V_2,V_4)	GED(V_2)[b]	GED(V_2,V_4)[b]	jet[c]
V_2/kJ mol^{-1}	3.6(4)	3.3(20)	2.5(4)	3.7(14)	2.41
V_4/kJ mol^{-1}	0[d]	0.6(32)	0[d]	−8.66[d]	0[d]
ΔA/J mol^{-1}	3027(2)	3027(2)			
η	−1.3(1)	−1.3(23)			

trans-Azobenzene

	NMR	GED[e]
V_2/kJ mol^{-1}	25[f]	8.8(33)
V_4/kJ mol^{-1}	1.7[d]	1.7(59)
ΔA^g/J mol^{-1}	3075(5)	
η^g	−1.2(1)	
$\Delta A_{NN}{}^g$/J mol^{-1}	11(13)	

[a] The values in parentheses are σ. [b] Gas electron diffraction data, ref 13. [c] Reference 12. [d] Assumed. [e] Reference 6. [f] See the text for the error. [g] The values were calculated by assuming V_2 and V_4 to be 25 and 1.7 kJ mol^{-1}, respectively.

In the present study of tolan, the determined value of V_4 is not significantly different from zero, as shown in Table 4. Thus, the determined V_2 value is essentially the same as that obtained by assuming V_4 to be zero. The analysis including only the V_2 term is consistent with the corresponding analyses of the data of jet spectroscopy[12] and GED.[13] Thus, the equilibrium structure of tolan is planar in ZLI 1132 as in the gas and solid phases. The result of GED analysis[13] considering the V_4 term is considered as a false solution. In Figure 3, the probability distribution function of the conformer is plotted against the dihedral angle.

Conformation of *trans*-Azobenzene. The molecular structure of *trans*-azobenzene is planar according to recent studies by GED[6b] and most ab initio and DFT calculations,[6,28] except MP2/6-31+G** calculations.[28] About two decades ago, the nonplanar structure with C_2 or C_i symmetry was reported for *trans*-azobenzene[29] where the internal rotation of each phenyl ring was treated as a small amplitude vibration. The result of our recent study[6b] is reliable because the internal rotation of each phenyl ring is treated as a large amplitude vibration taking

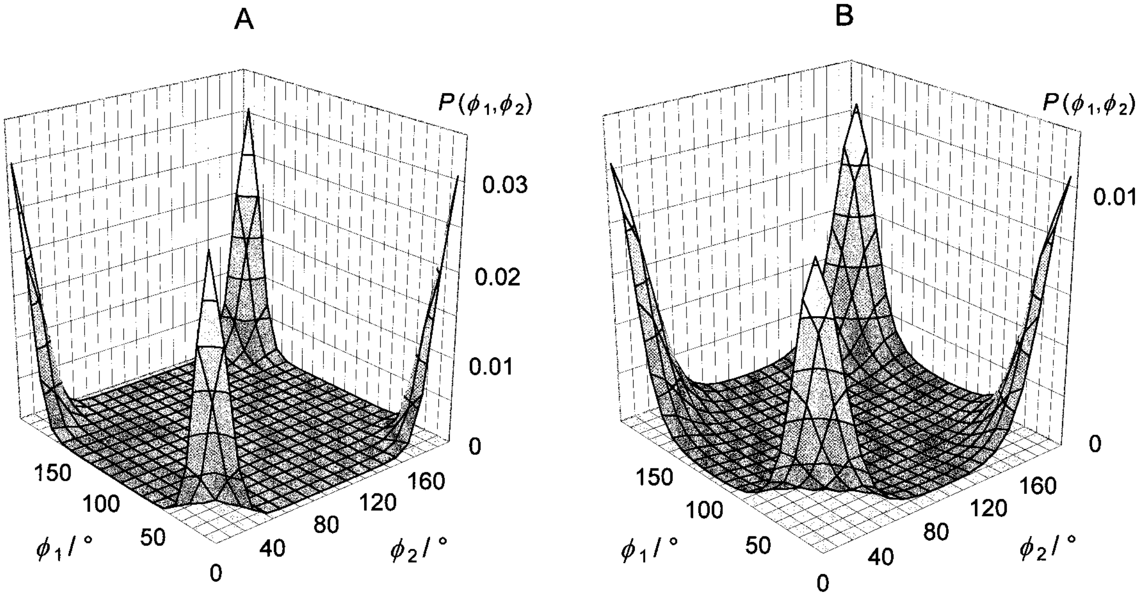

Figure 4. Probability distribution functions, $P(\phi_1,\phi_2)$, of *trans*-azobenzene obtained by liquid-crystal NMR (A) and gas electron diffraction (B).

account of a nonclassical effect. In the crystal, the torsional angle of the C−N═N−C plane against the phenyl rings takes values between 10° and 20°, depending on the temperature.[27b]

In ZLI 1132, the V_4 of *trans*-azobenzene was assumed to be 1.7 kJ mol^{-1} referring to the result of GED[6b] because it could not be determined. Although the V_2 of 25 kJ mol^{-1} minimizes RMS errors, the allowed value of V_2 is larger than 13 kJ mol^{-1} at the confidence interval of 99%. This means that the stable conformation is planar in ZLI 1132. Figure 4 displays the distribution function at 25 kJ mol^{-1}.

Comparison of Conformations. As mentioned above, the equilibrium structures of tolan and *trans*-azobenzene are planar in ZLI 1132 as in the gas phase. The dihedral angle around the O−Ph bond, ϕ, of phenyl benzoate is 66(+24, −14)°, 50°, and 67.5(2)° in the gas phase,[6c] in ZLI 1132[10] and in the crystal,[30] respectively. The dihedral angle around the Ph−C bond is zero both in the gas phase and in the liquid crystal, but it is 9.9(2)° in the crystal. The dihedral angle of biphenyl determined by NMR[8,9] is about 37° in each of liquid crystals I 35, ZLI 1115, and ZLI 1132 + EBBA (55:45 wt %). The dihedral angle is 44.4(12)° and 10° in the gas phase[31] and in the solid phase,[32] respectively. Thus, the equilibrium structures of four model compounds in liquid crystals are close to those in the gas phase.

The probability distribution functions $P(\phi)$ of four molecules are shown in Figure 3. The curves of biphenyl in liquid crystal, ZLI 1132 + EBBA (55:45 wt %), cited from ref 9 are shown in Figure 3.[33] The $P(\phi)$ of phenyl benzoate were derived from $V(\phi)$ neglecting $U(\{\phi\},\Omega)$ because the numerical data are not given in the literature.[10] The dependence of $P(\phi)$ on $U(\{\phi\},\Omega)$ is very small for each of tolan and *trans*-azobenzene as for 4-ethoxy-4′-cyanobiphenyl.[34] Each peak of the distribution curves of four compounds is narrower in liquid crystals than in the gas phase.

The distribution curves of phenyl benzoate show that this molecule takes a more planar conformation in ZLI 1132 than those in the gas phase. This is similar to the case of biphenyl.

These results are consistent with the difference in the rotational barriers at 90°. The rotational barriers, $V(90°)-V_{\min}(\phi)$, in liquid crystals are 3.6(4), 25, 4.1,[10] and 21[9] kJ mol^{-1} for tolan, *trans*-azobenzene, phenyl benzoate and biphenyl, respectively, whereas in the gas phase the corresponding rotational barriers are 2.5(4),[13] 7.9(33),[6b] 0.1,[6c] and 6.3[31] kJ mol^{-1}, respectively. Therefore, the rotational barrier of each compound is larger in liquid crystals than in the gas phase. This suggests that the liquid-crystal solvent stabilizes the planar or nearly planar conformations of solutes compared with perpendicular conformations. The present study provides fundamental structural and orientational data for liquid crystals with the cores of tolan and *trans*-azobenzene.

Conclusion

Conformations of tolan and *trans*-azobenzene are planar in liquid crystal ZLI 1132 as in the gas phase. The probability distribution functions of tolan, *trans*-azobenzene and phenyl benzoate are more localized in the liquid crystal than in the gas phase as in the case of biphenyl. The rotational barrier of each model compound at the dihedral angle of 90° is higher in the liquid crystal than in the gas phase. It can be explained if we assume that the liquid-crystal solvent stabilizes the planar or nearly planar structures of solutes. The present study suggests that the core of the liquid-crystal molecule, $RC_6H_4XC_6H_4R'$, has a conformation similar to that of the model compound and has a more restricted rotation in the liquid-crystal phase than in the gas phase.

Acknowledgment. We thank the High-Resolution NMR laboratory, Graduate School of Science, Hokkaido University, for the measurement of NMR spectra and the Computer Center, Institute for Molecular Science, Okazaki National Research Institutes, for the use of the NEC HPC computer and Library program GAUSSIAN 94. Numerical computations were carried out on the Hitachi Model MP5800/160 at the Hokkaido University Computing Center.

Supporting Information Available: Optimized geometrical parameters (Table S1 and Figure S1), local symmetry coordinates (Table S2), valence force field (Table S3), and observed and calculated vibrational wavenumbers with potential energy distributions (Table S4) are given for tolan. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Kuze, N.; Ebizuka, M.; Fujiwara, H.; Takeuchi, H.; Egawa, T.; Konaka, S.; Fogarasi, G. *J. Phys. Chem. A* **1998**, *102*, 2080.

(2) Kuze, N.; Fujiwara, H.; Takeuchi, H.; Egawa, T.; Konaka, S.; Fogarasi, G. *J. Phys. Chem. A* **1999**, *103*, 3054.

(3) Gray, G. W. *The Molecular Physics of Liquid Crystals*; Luckhurst G. R., Gray, G. W., Eds.; Academic Press: London, 1979; Chapter 1.

(4) Verbit, L.; Tuggey, R. L. *Liquid Crystals and Ordered Fluids*; Johnson, J. F., Porter, R. S., Eds.; Plenum Press: New York, 1973; Vol. 2, p 307.

(5) van der Veen, J.; de Jeu, W. H.; Grobben, A. H.; Boven, J. *Mol. Cryst. Liq. Cryst.* **1972**, *17*, 291.

(6) (a) Tsuji, T. Doctoral thesis presented to Graduate School of Science, Hokkaido University, Sapporo, 1999. (b) Tsuji, T.; Takashima, H.; Takeuchi, H.; Egawa, T.; Konaka, S., submitted for publication. (c) Tsuji, T.; Takeuchi, H.; Egawa, T.; Konaka, S. *J. Am. Chem. Soc.*, in press.

(7) Tsuji, T.; Takashima, H.; Takeuchi, H.; Egawa, T.; Konaka, S. *J. Mol. Struct.* **2000**, *554*, 203.

(8) Celebre, G.; De Luca, G.; Longeri, M.; Catalano, D.; Veracini, C.; Emsley, J. W. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 2623.

(9) Chandrakumar, T.; Polson, J. M.; Burnell, E. E. *J. Magn. Reson.* **1996**, *A118*, 264.

(10) Emsley, J. W.; Furby, M. I. C.; De Luca, G. *Liq. Cryst.* **1996**, *21*, 877.

(11) Takeuchi, H.; Inoue, K.; Ando, Y.; Konaka, S. *Chem. Lett.* **2000**, 1300.

(12) Okuyama, K.; Hasegawa, T.; Ito, M.; Mikami, N. *J. Phys. Chem.* **1984**, *88*, 1711.

(13) Abramenkov, A. V.; Almenningen, A.; Cyvin, B. N.; Cyvin, S. J.; Jonvik, T.; Khaikin, L. S.; Rømming C.; Vilkov, L. V. *Acta Chem. Scand.* **1988**, *42*, 674.

(14) Hasegawa, M. *Ekisyo* **1999**, *3*, 3.

(15) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 94*, Revision D.3; Gaussian, Inc.: Pittsburgh, PA, 1995.

(16) The theoretical value of $E(90°) - E(0°)$ in tolan is 1.7, 2.1 and 4.2 kJ mol^{-1}, respectively, according to RHF, MP2 and BP86 calculations using the basis set 6-31G**.

(17) (a) Baranovic, G.; Colombo, L.; Skare, D. *J. Mol. Struct.* **1986**, *147*, 275. (b) Kellerer, B.; Hacker, H. H. *J. Mol. Struct.* **1972**, *13*, 79. (c) Bobrov, A. V.; Sterin, K. E. *Opt. Spectrosc.* **1964**, *17*, 625.

(18) Celebre, G.; Castiglione, F.; Longeri, M.; Emsley, J. W. *J. Magn. Reson. A* **1996**, *121*, 139.

(19) Wright, A. H. *Foundations of Genetic Algorithms*; Rawlins, G. J. E., Ed.; Morgan Kaufmann Publishers: San Mateo, 1991; p 205.

(20) *R*-value is defined by $\{\Sigma_i(I_i^{obs} - I_i^{calc})^2/(I_i^{obs})^2\}^{1/2}$, where I_i is the *i*th intensity.

(21) This term arises because the internal rotation should not cause the whole molecular rotation. Hadder, J. E.; Frederick, J. H. *J. Chem. Phys.* **1992**, *97*, 3500.

(22) Egawa, T.; Konaka, S., unpublished.

(23) Niederberger, W.; Diehl, P.; Lunazzi, L. *Mol. Phys.* **1973**, *26*, 571.

(24) It is interesting to discuss the influence of vibrational corrections for these constants on conformational analysis. The vibrational corrections for D_{16}, D_{17}, and D_{27} are 2, 0.3, and 0.3%, respectively. According to Diehl, the neglect of the vibrational corrections introduces errors of 0.7, 0.1, and

0.1% for r_{16}, r_{17}, and r_{27}, respectively (Diehl, P. *Accurate Molecular structure*; Domenicano, A., Hargittai, I., Eds.; Oxford University Press: Oxford, 1992; Chapter 12). Thus, the conformational analysis is considered to be slightly affected by the corrections.

(25) Lounila, J.; Diehl, P. *Mol. Phys.* **1984**, *52*, 827.

(26) (a) Espiritu, A. A.; White, J. G. *Z. Kristallogr.* **1978**, *147*, 177. (b) Mavridis, A.; Moustakali-Mavridis, I. *Acta Crystallogr.* **1977**, *B33*, 3612. (c) Samarskaya, V. D.; Myasnikova, R. M.; Kitaigorodskii, A. I. *Kristallogr.* **1968**, *13*, 616.

(27) (a) Brown, C. J. *Acta Crystallogr.* **1966**, *21*, 146. (b) Harada, J.; Ogawa, K.; Tomoda, S. *Acta Crystallogr.* **1997**, *B53*, 662. (c) Bouwstra, J. A.; Schouten, A.; Kroon, J. *Acta Crystallogr.* **1983**, *C39*, 1121.

(28) Kurita, N.; Tanaka, S.; Itoh, S. *J. Phys. Chem. A* **2000**, *104*, 8114.

(29) Traetteberg, M.; Hilmo, I.; Hagen, K. *J. Mol. Struct.* **1977**, *39*, 231.

(30) Shibakami, M.; Sekiya, A. *Acta Crystallogr.* **1995**, *C51*, 326.

(31) Almenningen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J.; Samdal, S. *J. Mol. Struct.* **1985**, *128*, 59.

(32) Cailleau, H.; Baudour, J. L.; Zeyen, C. M. E. *Acta Crystallogr.* **1979**, *B35*, 426.

(33) Figure 4 in ref 9 shows that the $P(\phi)$ values in ZLI 1132 + EBBA (55:45 wt %), I 35,[8] and ZLI 1115[8] are not significantly different from one another.

(34) Emsley, J. W.; Horne, T. J.; Celebre, G.; Longeri, M.; Zimmermann, H. *J. Phys. Chem.* **1992**, *96*, 7929.