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Effects of Molecular Structure on the Stability of a Thermotropic Liquid Crystal. Gas Electron Diffraction Study of the Molecular Structure of Phenyl Benzoate

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Abstract: As a model of the core of molecules forming liquid crystals, the molecular structure of phenyl benzoate (Ph−C(=O)−O−Ph) at 409 K was determined by gas electron diffraction, and the relationship between the gas-phase structures of model compounds and the nematic-to-liquid transition temperatures was studied. Structural constraints were obtained from RHF/6-31G** ab initio calculations. Vibrational mean amplitudes and shrinkage corrections were calculated from the harmonic force constants given by normal coordinate analysis. Thermal vibrations were treated as small-amplitude motions, except for the phenyl torsion, which was treated as a large-amplitude motion. The potential function for torsion was assumed to be $V(\phi_1,\phi_2) = V_{12}(1 - \cos 2\phi_1)/2 + V_{14}(1 - \cos 4\phi_1)/2 + V_{22}(1 - \cos 2\phi_2)/2$, where ϕ_1 and ϕ_2 denote the torsional angles around the C−Ph and O−Ph bonds, respectively. The potential constants (V_{ij}/kcal mol^{-1}) and the principal structure parameters (r_g/Å, $\angle_\alpha$/deg) with the estimated limits of error (3σ) are as follows: $V_{12} = -1.3$ (assumed); $V_{14} = -0.5(9)$; $V_{22} = 3.5(15)$; $r(\mathrm{C{=}O}) = 1.208(4)$; $r(\mathrm{C({=}O){-}O}) = 1.362(6)$; $r(\mathrm{C({=}O){-}O}) - r(\mathrm{O{-}C}) = -0.044$ (assumed); $r(\mathrm{C({=}O){-}C}) = 1.478(10)$; $\langle r(\mathrm{C{-}C})\rangle = 1.396(1)$; $\angle\mathrm{OCO} = 124.2(13)$; $\angle\mathrm{O{=}CC} = 127.3(12)$; $\angle\mathrm{COC} = 121.4(22)$; $(\angle\mathrm{OCC_{cis}} - \angle\mathrm{OCC_{trans}})/2 = 3.0(15)$; $(\angle\mathrm{C({=}O)CC_{cis}} - \angle\mathrm{C({=}O)CC_{trans}})/2 = 4.8(17)$, where $\langle\ \rangle$ means an average value and $\mathrm{C{-}C_{cis}}$ and $\mathrm{C{-}C_{trans}}$ bonds are cis and trans to the C(=O)−O bond, respectively. The torsional angle around the O−Ph bond was determined to be 64(+26,−12)°. An apparent correlation was found between the contributions of the cores to the clearing point of liquid crystals and the gas-phase structures of model compounds of the cores of mesogens, i.e., phenyl benzoate, *trans*-azobenzene (*t*-AB), *N*-benzylideneaniline, *N*-benzylideneaniline *N*-oxide (NBANO), *trans*-azoxybenzene (*t*-AXB), and *trans*-stilbene. The structures of *t*-AB, NBANO, and *t*-AXB have been obtained by our research group.

Introduction

Phenyl benzoate (PB, Figure 1) is a model of molecular cores of compounds capable of forming liquid crystals (mesogen) of $X{-}C_6H_4{-}Y{-}C_6H_4{-}Z$ type, where Y is the linking unit and X and Z denote terminal groups.[1] The moiety of $-C_6H_4{-}Y{-}C_6H_4-$ is the core in this case. It is known from experience that the nematic-to-liquid phase transition temperature (T_{NI}) of liquid crystals containing two phenylene rings generally decreases in the following order of linking units:[1,2]

$$\begin{aligned}&-\mathrm{CH{=}CH}- > -\mathrm{N{=}N(O)}- > -\mathrm{CH{=}N(O)}- >\\ &\qquad -\mathrm{N{=}N}- > -\mathrm{CH{=}N}- > -\mathrm{COO}-\end{aligned} \tag{1}$$

On the basis of chemical formulas, Knaak et al.[2] evaluated the contributions of the linking unit and the terminal substituents to T_{NI}. They expressed the T_{NI} of mesogen of that type as

$$T_{NI} = \Delta T(\mathrm{X}) + \Delta T(\mathrm{Y}) + \Delta T(\mathrm{Z}) \tag{2}$$

and determined the substituent constants of the linking unit, $\Delta T(\mathrm{Y})$, and the terminal groups, $\Delta T(\mathrm{X})$ and $\Delta T(\mathrm{Z})$. Recently, some additional constants have been evaluated by Thiemann and Vill.[3] The determined $\Delta T(\mathrm{Y})$ values are $\Delta T(-\mathrm{CH{=}CH}-) = 27.6$ °C, $\Delta T(-\mathrm{N{=}N(O)}-) = 13.9$ °C, $\Delta T(-\mathrm{CH{=}N(O)}-) = 8.7$ °C, $\Delta T(-\mathrm{N{=}N}-) = -3.5$ °C, $\Delta T(-\mathrm{CH{=}N}-) = -9.0$ °C, and $\Delta T(-\mathrm{COO}-) = -30.5$ °C.

Because the shape of constituent molecules is an important factor in forming the liquid crystal phase,[4] it is interesting to investigate the relationship between the molecular structure and the T_{NI} value of the mesogen, which is related to the stability of the liquid crystal. Investigations on such a relationship have so far been made on the basis of crystal data, and the results have been summarized by Gray.[4] The structure of the molecule in the crystal often differs from that of the isolated molecule. Such a relationship based on the structures of isolated molecules has not previously been reported. Therefore, it is worthwhile to investigate the relationship between the gas-phase structure and the T_{NI} value of the mesogen.

Recently we determined the gas-phase structures of mesogens *p*-azoxyanisole[5] and 4-methoxybenzylidene-4′-*n*-butylaniline[6] by gas electron diffraction (GED). The results suggest that the structure of the core of the mesogenic molecule is in most cases

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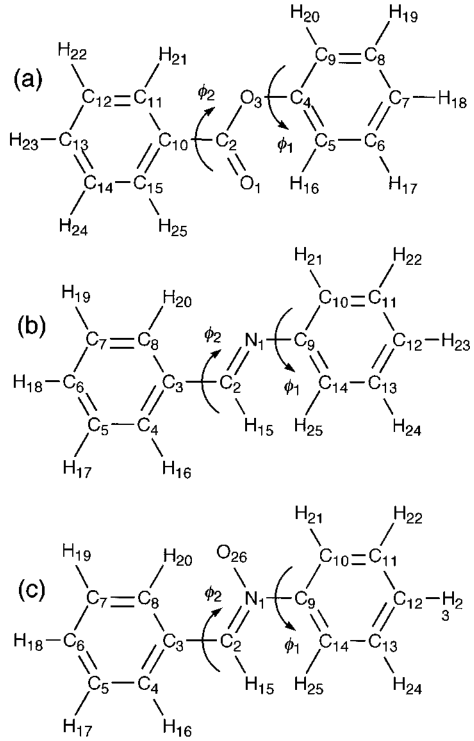

Figure 1. Molecular model with atom numbering of phenyl benzoate (a), *N*-benzylideneaniline (b), and *N*-benzylideneanline *N*-oxide (c). In phenyl benzoate, ϕ_1 and ϕ_2 denote dihedral angles $C_2O_3C_4C_5$ and $O_3C_2C_{10}C_{11}$, respectively. In *N*-benzylideneaniline and *N*-benzylideneanline *N*-oxide, ϕ_1 and ϕ_2 denote dihedral angles $C_2N_1C_9C_{14}$ and $N_1C_2C_3C_8$, respectively. They are defined to be 0° for the cis conformer shown here and are measured clockwise.

almost the same as that of its model compound in the gas phase. Although structure determinations of mesogens in the gas phase are quite difficult, requiring a very long time, it is relatively easy to determine the gas-phase structures of the model compounds of cores. The liquid crystals with the core of PB type are known to have clearing points lower than the other types of liquid crystals, as reported in ref 3. Thus, it is necessary to know the structure of PB to investigate the relationship between the structure and the clearing point.

The crystal structure of PB was determined by X-ray diffraction[7,8] at room temperature. It was found that the phenyl ring bonded to an oxygen atom rotates around the O−Ph bond by about 70°, and the other ring rotates by about 10° in the opposite direction from the planar structure. Le Févre and Sundaram measured the molar Kerr constant of PB in benzene solution.[9] They concluded that the rotational angle of the phenyl ring attached to the oxygen atom is about 70°. From normal coordinate analysis, the IR spectra of PB measured in the liquid state were ascribed to the conformer with the rotational angle of 67°.[10] Emsley et al.[11] analyzed the ^1H NMR spectrum of PB in nematic liquid crystal solvent, ZLI 1132, and determined the potential function for internal rotations around the O_3-C_4, C_2-C_{10}, and C_2-O_3 bonds. The determined potential function for the internal rotation around the O_3-C_4 bond has a minimum at about 50°.

Although the structure of PB was investigated widely in the condensed phase as described above, no structural data for the gas phase are available. The purpose of the present study is to determine the structure of PB by GED and to investigate the relationship between the structure and the clearing point. The structure determination of PB is difficult because there are many atom pairs with similar interatomic distances and internal rotations, although it may be much easier than the structure determination of the corresponding mesogens. In the present study, ab initio and density functional theory (DFT) calculations have been performed to obtain structural constraints, and the internal rotations of phenyl rings have been treated as large-amplitude motions. Ab initio calculations have also been performed for *N*-benzylideneaniline (NBA) and *N*-benzylideneaniline *N*-oxide (NBANO) for comparison.

Experimental Section

Commercial samples with a purity of better than 99% (Tokyo Chemical Industry Co., Ltd.) were used without further purification. Electron diffraction patterns were recorded on 8- × 8-in. Kodak projector slide plates by using an apparatus equipped with an r^3 sector.[12] A high-temperature nozzle was used to vaporize the sample.[5] The temperature of the nozzle tip was set at about 409 K during exposures. The accelerating voltage of incident electrons was about 38 kV. The diffraction patterns of carbon disulfide were recorded in the same sequence of exposures as the sample. The scale factor was calibrated to the known bond length of CS_2 (r_a(C−S) = 1.5570 Å).[13] Other experimental conditions are as follows: camera distance, 244.4 mm; uncertainty of the scale factor (3σ), 0.04%; exposure time, 64−74 s; beam current, 1.55 μA; background pressure, 4×10^{-6} Torr.

Data reduction was performed as described in the literature.[14] Total intensities from four photographic plates were averaged and used in the data analysis. Total intensities and backgrounds are deposited as Supporting Information (Table S1). Elastic atomic scattering factors were calculated as described in ref 15, and inelastic ones were taken from ref 16.

Theoretical Calculations

Phenyl Benzoate. Structural parameters were optimized by RHF/6-31G** ab initio and BP86/6-31G** DFT calculations by using the programs GAUSSIAN 92 and GAUSSIAN 94.[17,18] Optimized structural parameters are listed in Table 1. The structure optimized by the RHF/6-31G** calculation has C_s symmetry, where the ring bonded to the O_3 atom is perpendicular to the rest of the molecule. The dihedral angles, ϕ_1 and

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Table 1. Results of the Geometry Optimizations of Phenyl Benzoate by RHF/4-31G**, RHF/6-31G**, and BP86/6-31G** Calculations[a]

	RHF/4-31G**	RHF/6-31G**	BP86/6-31G**		RHF/4-31G**	RHF/6-31G**	BP86/6-31G**
			Bond Lengths (Å)				
$O_1{=}C_2$	1.184	1.186	1.222	$C_{13}{-}C_{14}$	1.384	1.387	1.405
$C_2{-}O_3$	1.338	1.339	1.386	$C_{14}{-}C_{15}$	1.380	1.382	1.400
$O_3{-}C_4$	1.381	1.383	1.403	$C_{15}{-}C_{10}$	1.388	1.390	1.411
$C_2{-}C_{10}$	1.487	1.489	1.493	$C_5{-}H_{16}$	1.073	1.075	1.090
$C_4{-}C_5$	1.379	1.380	1.404	$C_6{-}H_{17}$	1.075	1.075	1.095
$C_5{-}C_6$	1.381	1.385	1.404	$C_7{-}H_{18}$	1.075	1.075	1.094
$C_6{-}C_7$	1.384	1.385	1.404	$C_8{-}H_{19}$	1.075	1.075	1.095
$C_7{-}C_8$	1.382	1.385	1.404	$C_9{-}H_{20}$	1.074	1.075	1.094
$C_8{-}C_9$	1.383	1.385	1.402	$C_{11}{-}H_{21}$	1.072	1.073	1.092
$C_9{-}C_4$	1.377	1.380	1.403	$C_{12}{-}H_{22}$	1.075	1.075	1.095
$C_{10}{-}C_{11}$	1.387	1.390	1.411	$C_{13}{-}H_{23}$	1.076	1.076	1.095
$C_{11}{-}C_{12}$	1.381	1.384	1.401	$C_{14}{-}H_{24}$	1.075	1.075	1.095
$C_{12}{-}C_{13}$	1.383	1.386	1.405	$C_{15}{-}H_{25}$	1.073	1.074	1.094
			Bond Angles (deg)				
$O_1C_2O_3$	123.5	123.3	124.4	$C_{12}C_{13}C_{14}$	120.3	120.3	120.1
$C_2O_3C_4$	120.2	119.3	121.2	$C_{13}C_{14}C_{15}$	119.8	119.9	120.0
$O_1C_2C_{10}$	124.3	124.4	124.9	$C_{14}C_{15}C_{10}$	120.1	120.0	120.1
$O_3C_4C_9$	117.9	119.2	115.1	$C_{15}C_{10}C_{11}$	120.0	120.0	119.8
$O_3C_4C_5$	120.7	119.2	123.5	$C_4C_5H_{16}$	119.9	119.7	120.4
$C_2C_{10}C_{11}$	122.3	122.3	122.9	$C_5C_6H_{17}$	119.5	119.6	119.0
$C_2C_{10}C_{15}$	117.7	117.7	117.3	$C_6C_7H_{18}$	120.1	120.1	120.2
$C_4C_5C_6$	119.0	119.0	118.5	$C_7C_8H_{19}$	120.2	120.1	120.3
$C_5C_6C_7$	120.4	120.3	121.0	$C_8C_9H_{20}$	121.4	121.3	121.5
$C_6C_7C_8$	119.8	119.8	119.6	$C_{10}C_{11}H_{21}$	119.9	119.9	119.5
$C_7C_8C_9$	120.2	120.3	120.2	$C_{11}C_{12}H_{22}$	119.9	119.9	119.8
$C_8C_9C_4$	119.2	119.0	119.4	$C_{12}C_{13}H_{23}$	119.8	119.9	119.9
$C_9C_4C_5$	121.4	121.5	121.3	$C_{13}C_{14}H_{24}$	120.2	120.2	120.1
$C_{10}C_{11}C_{12}$	119.8	119.8	119.8	$C_{14}C_{15}H_{25}$	121.0	121.0	121.5
$C_{11}C_{12}C_{13}$	120.0	120.0	120.2				
			Dihedral Angles (deg)[b]				
$C_2O_3C_4C_5$ (ϕ_1)	70.3	91.7	41.3	$C_{10}C_2O_3C_4$	179.0	180.0	−179.6
$O_3C_2C_{10}C_{11}$ (ϕ_2)	0.6	−0.0	1.7	$O_3C_4C_9C_8$	−176.5	−176.8	−176.3
$O_1C_2O_3C_4$	−1.0	−0.0	0.6	$O_3C_4C_5C_6$	176.5	176.8	176.1

[a] See Figure 1 for atom numbering. [b] Only relatively important dihedral angles are listed.

ϕ_2, are defined as $C_2O_3C_4C_5$ and $O_3C_2C_{10}C_{11}$, respectively. They are 0° at the cis configuration and are measured clockwise. The $C_4{\cdots}C_7$ diagonal is not collinear to the $O_3{-}C_4$ bond but tilts very slightly away from the O_1 atom, and hence the torsional angle ϕ_1 is not 90° but 91.7°. It differs from 84°, value which was obtained from the RHF/6-31G* calculations performed by Sun.[19] Thus, RHF/4-31G** calculations were also performed to investigate the dependence of the torsional angle ϕ_2 on the basis sets and resulted in C_1 symmetry with the torsional angle of 70°. On the other hand, BP86/6-31G** calculations gave a rather small value, 41°, for this angle.

PB has three degrees of freedom for internal rotations. The torsion around the $C_2{-}O_3$ bond in an ester group is known to be fairly rigid,[20,21] and it was taken as a small-amplitude motion in the present study. An approximate potential surface was obtained by RHF/6-31G** calculation. In the calculations, the torsional angles of the phenyl rings, ϕ_1 and ϕ_2, were fixed at arbitrarily selected values while the other geometrical parameters were optimized. The potential energy functions of ϕ_1 and ϕ_2 were calculated at intervals of 15° by RHF/6-31G** calculations. Figure 2 displays the calculated curves. The barrier heights for the $O_3{-}C_4$ and $C_2{-}C_{10}$ torsions are 1.3 and 8.1 kcal mol^{-1}, respectively. The calculated potential surface shows that the internal rotations of phenyl rings are almost independent. The results of the RHF/6-31G** calculations are listed in Tables S2−S4 in the Supporting Information.

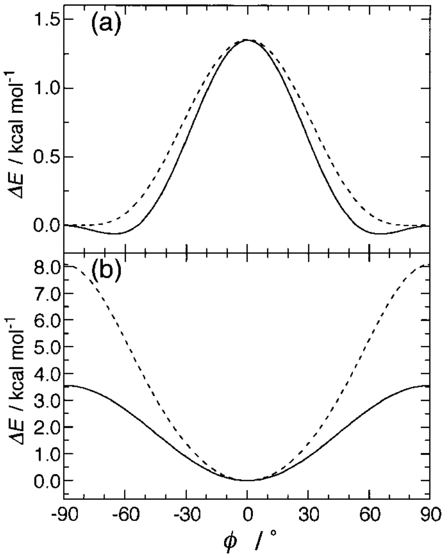

Figure 2. Experimental (solid curves) and theoretical (dashed curves) potential energy functions for the torsional motion of phenyl benzoate relative to the minimum value. Theoretical functions were given by RHF/6-31G** calculations. (a) The potential function for torsion about the $O_3{-}C_4$ bond when ϕ_2 is fixed at 0°. (b) The potential function for torsion about the $C_2{-}C_{10}$ bond when ϕ_1 is fixed at 0°. The vertical scale is different from that in (a).

The Cartesian force constants of PB obtained by BP86/6-31G** calculations were converted to the force constants in internal coordinates. Most of the calculated wavenumbers are in good agreement with the wavenumbers observed in the liquid

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state[10] without modifying force constants. However, no experimental wavenumbers of C−H stretching vibrations are available. Therefore, the theoretical force constants relating to C−H stretching modes were modified by a scale factor[22] of 0.964, which is the value used for the corresponding force constants of *trans*-azobenzene and *trans*-azoxybenzene. Symmetry coordinates, scaled force constants, and observed and calculated wavenumbers are listed in Tables S5−S7 in the Supporting Information.

***N*-Benzylideneaniline and *N*-Benzylideneaniline *N*-Oxide.** No experimental structure is available for *N*-benzylideneaniline *N*-oxide (NBANO). On the other hand, the molecular structure of *N*-benzylideneaniline (NBA), which is one of the compounds related to NBANO, was determined by Traetteberg et al.[23] by GED. As shown in Figure 1, NBANO differs from NBA only by the existence of the oxygen atom bonded to the nitrogen atom. Therefore, it is expected that the molecular structure of NBANO can be predicted from the experimental structure of NBA and the theoretical difference between the structures of NBA and NBANO.

Geometries were optimized by RHF/6-31G** calculations. First, the potential curve for the torsions of phenyl rings was calculated, and only one stable conformer was found for NBA and NBANO. Thus, all structural parameters were optimized for NBA and NBANO. The resulting parameters of stable conformers are listed in Table 2. The energies and optimized parameters of the stable conformers and pseudoconformers are deposited as Supporting Information (Tables S8−S11). The torsional angles of the phenyl rings, ϕ_1 and ϕ_2, of NBA were calculated to be 45° and 2°, respectively. The experimental values of ϕ_1 and ϕ_2 are 52(5)° and 0(15)°, respectively, where the numbers in parentheses are the estimated limits of error.[23] Therefore, the conformation of NBA given by RHF/6-31G** calculations almost agrees with the experimental one.

The molecular structure of NBANO was estimated as mentioned above. Because the bond lengths of NBA are given in r_a only,[23] those of NBANO are also given in r_a. Table 2 lists the estimated structural parameters of NBANO.

Analysis of Electron Diffraction Data

To reduce the number of adjustable structural parameters, data analysis was performed under the following assumptions: (1) the $C_{10}C_2(O_1)O_3C_4$ moiety is planar; (2) the $O_1{=}C_2$ bond is cis to the $O_3{-}C_4$ bond; (3) the differences between C−C bond lengths in the phenyl rings are equal to those given by RHF/6-31G** calculations; (4) the bond angles of the phenyl rings, $\angle C_5C_4C_9$, $\angle C_4C_5C_6$, $\angle C_4C_9C_8$, $\angle C_{11}C_{10}C_{15}$, $\angle C_{10}C_{11}C_{12}$, and $\angle C_{10}C_{15}C_{14}$, are equal to those given by RHF/6-31G** calculations; (5) the difference, $r_a(O_3{-}C_4) - r_a(C_2{-}O_3)$, is equal to 0.044 Å, a value given by RHF/6-31G** calculations; (6) hydrogen atoms lie on the bisector of the CCC angle; and (7) C−H bond lengths are the same. Assumption 2 is reasonable because only cis configuration is found for esters in the gas phase.[21,24,25]

To treat the internal rotation of two phenyl rings, 74 pseudoconformers, each of which has a different combination of ϕ_1 and ϕ_2 values, were taken into account. Dihedral angles were selected at intervals of 15° between −90° and 90°. It was assumed that the value of ϕ_2 is 0° at the potential minimum because of the conjugation between the carbonyl and phenyl groups. The RHF/6-31G** calculations show that the internal rotations around ϕ_1 and ϕ_2 are almost independent of each other. In addition, the flat bottom of the potential function for ϕ_1 shown in Figure 2a cannot be expressed with only one cosine term, while that for ϕ_2 has a simple sinusoidal shape. Therefore, the potential function was assumed to be

Table 2. Theoretical and Experimental Structures of *N*-Benzylideneaniline (NBA) and *N*-Benzylideneaniline *N*-Oxide (NBANO)[a]

	NBA		NBANO	
	RHF/6-31G** r_e, $\angle_e$	GED[b] r_a, $\angle_\alpha$	RHF/6-31G** r_e, $\angle_e$	estimated[c] r_a, $\angle_\alpha$
$r(N_1{=}C_2)$	1.255	1.284 (10)	1.280	1.309
$r(N_1{-}C_9)$	1.408	1.432 (15)	1.444	1.468
$r(C_2{-}C_3)$	1.477	1.440 (15)	1.462	1.425
$\langle r(C{-}C)_{ring}\rangle$[d]	1.387	1.398 (1)	1.387	1.398
$\langle r(C{-}H)\rangle$[d]	1.077	1.095 (10)	1.074	1.092
$r(N_1{-}O_{26})$			1.277	
$\angle N_1C_2C_3$	120.0	125.0 (15)	127.1	132.1
$\angle C_2N_1C_9$	122.8	115.0 (20)	120.0	112.2
$\angle N_1C_9C_{14}$	123.0	122.7 (20)	121.6	121.3
$\angle C_2C_3C_4$	119.3	120.0 (15)	116.3	117.0
$\angle O_{26}N_1C_2$			125.0	
$\phi_1(C_2N_1C_9C_{14})$	44.6	52 (5)	41.0	48
$\phi_2(N_1C_2C_3C_8)$	1.5	0 (15)	0.8	0

[a] Bond lengths in angstroms, angles in degrees. Atom numbering is shown in Figure 1. [b] Reference 23. Numbers in parentheses are the estimated limits of error referring to the last significant digits. [c] Estimated from the structurual parameters of NBA reported in ref 23 and the theoretical differences between the parameters of NBA and NBANO. See text for the details of the estimation. [d] Average value.

$$V(\phi_1,\phi_2) = V_{12}/2(1 - \cos 2\phi_1) + V_{14}/2(1 - \cos 4\phi_1) + V_{22}/2(1 - \cos 2\phi_2) \quad (3)$$

The relative abundance of each pseudoconformer was calculated according to the classical approximation. The differences in the structural parameters between pseudoconformers were fixed at the values of RHF/6-31G** calculations. As shown in the Theoretical Calculations section, the $O_3{-}C_4$ bond and the $C_4{\cdots}C_7$ diagonal are not collinear; hence, the internal rotation around the $O_3{-}C_4$ bond includes not only the change in the dihedral angle, ϕ_1, but also that in the tilt angle, which is defined as $(\angle_\alpha O_3C_4C_5 - \angle_\alpha O_3C_4C_9)/2$. This coupling was included in the analysis effectively by taking the dependence of the tilt angle on the dihedral angle into account. The internal rotation around the $C_2{-}C_{10}$ bond was treated in the same manner.

Vibrational mean amplitudes and shrinkage corrections for each pseudoconformer were calculated for the modified force constants. In this calculation, the contributions from the $O_3{-}C_4$ and $C_2{-}C_{10}$ torsions were not included because they were treated as large-amplitude vibrations. Calculated vibrational mean amplitudes are listed in Table S12. Mean amplitudes were refined in five groups in the data analysis as shown in that table. Shrinkage corrections were fixed at calculated values. The asymmetry parameters, κ, for bonded atom pairs were fixed at the values estimated by the conventional method,[26] while those for nonbonded atom pairs were assumed to be zero.

Structural parameters, mean amplitudes, potential parameters, and the index of resolution were determined by least-squares calculations on molecular scattering intensities.

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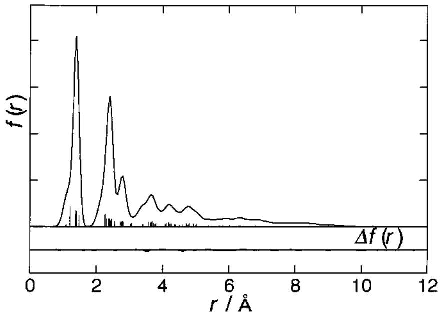

Figure 3. Experimental radial distribution curve of phenyl benzoate; $\Delta f(r) = f(r)^{\text{obs}} - f(r)^{\text{calc}}$. Vertical bars indicate relatively important atom pairs of the molecule.

Results and Discussion

Molecular scattering intensities and a radial distribution curve are displayed in Figures S1 and 3, respectively. The structural parameters and mean amplitudes determined are listed in Tables 3 and S12, respectively. The correlation matrix elements with absolute value larger than 0.7 are $r(\text{C}-\text{O})/r(\text{C}-\text{C})_{\text{ring}} = -0.92$; $\text{tilt}(\text{C}_4)/l_{ij}(\text{group 2}) = -0.87$. The correlation matrix is given in Table S13 as Supporting Information.

Conformation and Barrier to Internal Rotations. Three sets of analyses were performed to determine the potential parameters. In the first analysis, set 1, all of the potential parameters in eq 3 were refined. The resulting parameter values are as follows: $V_{12} = -1.2(1.2)$, $V_{14} = -0.4(1.4)$, and $V_{22} = 3.5(1.6)$ kcal mol^{-1}, where numbers in parentheses are 3 times the standard deviations. The uncertainties of V_{12} and V_{14} are large compared with their absolute values. In set 2, therefore, V_{14} was assumed to be zero, implying that the potential minimum is at $\phi_1 = 90°$ for the negative values of V_{12}. The result of the analysis is given in Table 3. The value of V_{12} determined, $-1.0(7)$ kcal mol^{-1}, agrees with the theoretical value given by RHF/6-31G** calculations, -1.3 kcal mol^{-1}, the latter being obtained from the energy difference between the $\phi_1 = 90°$ and $\phi_1 = 0°$ forms. In set 3, the value of V_{12} was fixed at this theoretical value. The value of V_{14} was determined to be $-0.5(9)$ kcal mol^{-1}. The structural parameters and the parameter of V_{22} obtained in three sets of analyses are similar. The result of set 3 was chosen to be the final one in the present study.

The potential function for the O_3-C_4 torsion is shown in Figure 2a. The position of the potential minimum is calculated to be 64^{+26}_{-12} °. The relative energy for the rotation of the phenyl ring bonded to O_3 atom is determined by two factors. One is the steric repulsion between the phenyl ring and the oxygen atom in the carbonyl group, and the other is the conjugation between the COO group and the phenyl ring. The former and the latter make the planar conformation unstable and stable, respectively. In other words, the barrier to planarity is brought about by the steric repulsion, and the hump at the perpendicular form is a consequence of the conjugation. This interpretation is consistent with the fact that, in the case of phenyl acetate, the barrier to the perpendicular form changes much more than the barrier to the planarity by the $\pi-\pi^*$ excitation of the phenyl ring, which primarily affects the conjugation.[27] The large torsional angle of the phenyl ring bonded to the O_3 atom of phenyl benzoate indicates that the steric effect is dominant.

As shown in Figure 2b, the experimental barrier height for the C_2-C_{10} torsion, 3.5(1.6) kcal mol^{-1}, is nearly half the theoretical value. Among the molecules containing a Ph−C(=O) bond, the experimental barrier heights for internal rotation are available for benzaldehyde,[28] benzoyl fluoride,[28−30] benzoyl chloride,[28] and acetophenone.[28] Barrier heights are between 3.1 and 4.9 kcal mol^{-1} for these molecules. They agree with the corresponding height in PB within the limits of error.

Table 3. Structural and Potential Parameters of the Pseudoconformer with $\phi_1 = 60°$ and $\phi_2 = 0°$ of Phenyl Benzoate[a]

	set 1		set 2		set 3	
$r_g(\text{O}_1{=}\text{C}_2)$	1.208 (4)		1.208 (4)		1.208 (4)	
$r_g(\text{C}_2-\text{O}_3)$	1.362	(7)	1.362	(6)	1.362	(6)
$r_g(\text{O}_3-\text{C}_4)$	1.405		1.405		1.405	
$r_g(\text{C}_2-\text{C}_{10})$	1.478 (10)		1.478 (10)		1.478 (10)	
$r_g(\text{C}_4-\text{C}_5)$	1.394	(1)	1.394	(1)	1.394	(1)
$r_g(\text{C}_5-\text{C}_6)$	1.395		1.395		1.395	
$r_g(\text{C}_6-\text{C}_7)$	1.395		1.395		1.395	
$r_g(\text{C}_7-\text{C}_8)$	1.396		1.396		1.396	
$r_g(\text{C}_8-\text{C}_9)$	1.397		1.397		1.397	
$r_g(\text{C}_9-\text{C}_4)$	1.391		1.391		1.391	
$r_g(\text{C}_{10}-\text{C}_{11})$	1.401		1.401		1.401	
$r_g(\text{C}_{11}-\text{C}_{12})$	1.396		1.396		1.396	
$r_g(\text{C}_{12}-\text{C}_{13})$	1.397		1.397		1.397	
$r_g(\text{C}_{13}-\text{C}_{14})$	1.398		1.398		1.398	
$r_g(\text{C}_{14}-\text{C}_{15})$	1.394		1.394		1.394	
$r_g(\text{C}_{15}-\text{C}_{10})$	1.402		1.402		1.402	
$\langle r_g(\text{C}-\text{H})\rangle^b$	1.096 (5)		1.096 (4)		1.096 (4)	
$\angle_\alpha \text{O}_1\text{C}_2\text{O}_3$	124.2 (14)		124.2 (14)		124.2 (13)	
$\angle_\alpha \text{C}_2\text{O}_3\text{C}_4$	121.3 (23)		121.0 (23)		121.4 (22)	
$\angle_\alpha \text{O}_1\text{C}_2\text{C}_{10}$	127.3 (12)		127.4 (12)		127.3 (12)	
$\text{tilt}(\text{C}_4)^c$	3.0 (15)		2.7 (12)		3.0 (15)	
$\text{tilt}(\text{C}_{10})^e$	4.8 (17)		4.7 (18)		4.8 (17)	
V_{12}	−1.2 (12)		−1.0 (7)		-1.3^d	
V_{14}	−0.4 (14)		0.0^d		−0.5 (9)	
V_{22}	3.5 (16)		3.5 (16)		3.5 (15)	
k^f	0.981 (9)		0.981 (9)		0.981 (9)	

[a] See Figure 1 for atom numbering. r_g in angstroms and $\angle_\alpha$ in degrees. Numbers in parentheses are the estimated limits of error (3σ). [b] Average value. [c] Defined as $\text{tilt}(\text{C}_4) = (\angle_\alpha \text{O}_3\text{C}_4\text{C}_5 - \angle_\alpha \text{O}_3\text{C}_4\text{C}_9)/2$. [d] Assumed value. [e] Defined as $\text{tilt}(\text{C}_{10}) = (\angle_\alpha \text{C}_2\text{C}_{10}\text{C}_{11} - \angle_\alpha \text{C}_2\text{C}_{10}\text{C}_{15})/2$. [f] The index of resolution.

Table 4. Molecular Structures of Phenyl Benzoate (PB), Methyl Benzoate (MB), and Phenyl Acetate (PA)[a]

	PB		MB^b		PA^c	PB (crystal)
$r(\text{C}{=}\text{O})$	1.208 (4)		1.206 (3)		1.203 (5)	1.195 (2)
$r(\text{C}({=}\text{O})-\text{O})$	1.362	(6)	1.345	(4)	1.363 (10)	1.351 (2)
$r(\text{O}-\text{C})$	1.405		1.437		1.407 (12)	1.415 (2)
$r(\text{C}({=}\text{O})-\text{C})$	1.478 (10)		1.484 (6)		1.479 (11)	1.481 (2)
$\langle r(\text{C}-\text{C})_{\text{ring}}\rangle^d$	1.396 (1)		1.400 (1)		1.394 (3)	1.376 (3)
$\angle \text{O}{=}\text{C}-\text{O}$	124.2 (13)		123.0 (6)		127.4 (14)	123.1 (2)
$\angle \text{O}{=}\text{C}-\text{C}$	127.3 (12)		122.9 (9)		126.6 (15)	125.4 (2)
$\angle \text{C}-\text{O}-\text{C}$	121.4 (22)		116.8^e		122.5 (16)	118.1 (1)
$\text{tilt}(\text{C}_4)^f$	3.0 (15)				1.7 (19)	2.2 (1)
$\text{tilt}(\text{C}_{10})^g$	4.8 (17)		0.0 (8)			2.0 (1)
ϕ_1	64^{+26}_{-12}				62.9 (38)	67.5 (2)
ϕ_2	0^e		0^e			9.9 (2)

[a] See Figure 1 for atom numbering. r_g in angstroms and $\angle_\alpha$ in degrees for PB, MB, and PA. r_α structue for PB in the crystal state. Numbers in parentheses are the estimated limits of error (3σ). [b] Reference 31. [c] Reference 32. [d] Average value. [e] Assumed value [f] Defined as $\text{tilt}(\text{C}_4) = (\angle_\alpha \text{O}_3\text{C}_4\text{C}_5 - \angle_\alpha \text{O}_3\text{C}_4\text{C}_9)/2$ in phenyl benzoate. [g] Defined as $\text{tilt}(\text{C}_{10}) = (\angle_\alpha \text{C}_2\text{C}_{10}\text{C}_{11} - \angle_\alpha \text{C}_2\text{C}_{10}\text{C}_{15})/2$ in phenyl benzoate.

Geometrical Parameters. In Table 4, principal structural parameters are compared with those of methyl benzoate (MB)[31] and phenyl acetate (PA).[32] Most of the structure parameters of PB agree with those of MB and PA within the limits of error.

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The error limits given for the present result were estimated as 3 times the standard deviations (3σ) of the least-squares fitting. Another potential source of uncertainty is the inaccuracy of the theoretical calculations used for the structural constraints in the analysis (assumptions 3−5 and the structural changes among the pseudoconformers), the estimation of which is not straightforward. The structural parameters of the RHF method, in general, differ significantly from those of more sophisticated methods such as MP2. However, the differences among the similar structural parameters (e.g., C−C bond distances in the phenyl ring) show only a small dependence on the calculation methods, which are usually below the amount of the present error estimation (see our previous study as an example[33]). Therefore, it can be said that the present error estimation (3σ) covers not only the statistical error but also the systematic one in the assumptions.

The C(=O)−O bond length is close to that of PA and longer than that of MB. This bond length is known to be very sensitive to the substituent attached to the oxygen atom and decreases if the substituent is a *tert*-butyl or isopropyl group, which has an electron-releasing property.[14,34,35] Thus, the phenyl group is considered to be an electron-withdrawing substituent as compared with the methyl group.

In the crystal,[8] the dihedral angles around O−Ph and C−Ph bonds of PB are 67.5(2)° and 9.9(2)°, respectively. The latter angle is affected by the crystal packing. The bond lengths and angles agree with gas-phase values within 0.02 Å and 3°, respectively.

Factors Determining the Clearing Point of the Liquid Crystal. Van der Veen et al.[36] considered the dipole moment and the planarity of cores as the factors determining T_{NI} and stated that the former is more important. On the other hand, Verbit et al.[37] argued that the increase in the length of the linking unit increases T_{NI}. It is, however, pointed out that other factors such as rigidity, linearity, and conformation are also important.[4,36,37] In the present study, the conformations and the length of the linking units, r_{LU}, of the model compounds of the cores with the linking units in (1) were summarized in Figure 4. Structural data for *trans*-stilbene and *N*-benzylideneaniline are taken from refs 38 and 23, respectively, whereas the data for *trans*-azoxybenzene and *trans*-azobenzene are obtained from our investigations.[39,40] The structures of *trans*-stilbene (*t*-SB), *trans*-azoxybenzene (*t*-AXB), and *trans*-azobenzene (*t*-AB) are planar. Among the mesogens with the cores of the types *t*-SB, *t*-AXB, and *t*-AB, the clearing points decrease in the following order of the types of cores:

$$t\text{-SB} > t\text{-AXB} > t\text{-AB}$$

The values of r_{LU} increase in the same order, but the relationship between the substituent constant, ΔT(Y), and the length of the linking unit is not linear as in Figure 4. For example, the data point for *t*-AXB is much higher than the line connecting the points for *t*-AB and *t*-SB. This can be explained as follows. The coordinated oxygen atom in *t*-AXB has a fairly large negative charge, which is −0.59 *e* according to RHF/6-31G** calculations. Such a charged atom is considered to lead to additional intermolecular interactions, such as dipolar interactions, and is expected to raise the clearing point.

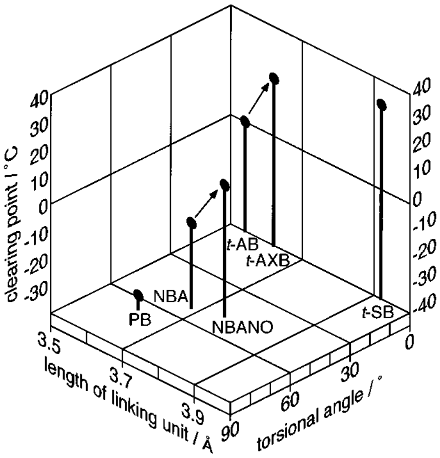
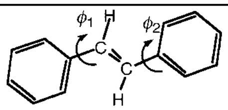
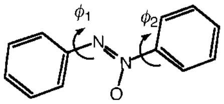
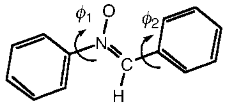
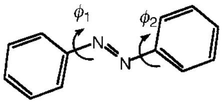
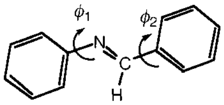
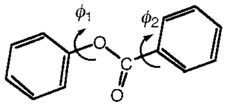


Figure 4. Substituent constants of the linking unit, ΔT(Y), plotted against the larger torsional angle of phenyl rings and the length of the linking unit of the model compound of the core. Arrows indicate the coordination of the nitrogen to the oxygen atom.

Table 5. Rotational Barriers for the Internal Rotation of Phenyl Rings (in kcal mol^{-1})

		ΔV_1[a]	ΔV_2[a]
t-SB		2.5[b]	2.5[b]
t-AXB		3.5	1.7
NBANO[c]		(2.6)[d]	(7.2)[d]
t-AB		1.9	1.9
NBA[c]		(1.4)[d]	(7.0)[d]
PB[c]		0.1	3.5

[a] ΔV_1 and ΔV_2 denote $\{V(90°,\phi_2^{e}) - V(\phi_1^{e},\phi_2^{e})\}$ and $\{V(\phi_1^{e},90°) - V(\phi_1^{e},\phi_2^{e})\}$, respectively. Here, ϕ_1^{e} and ϕ_2^{e} denote the values of ϕ_1 and ϕ_2 giving the potential minimum, respectively. [b] Calculated from the following potential function: $V(\phi_1,\phi_2) = -2.21(2 - \cos 2\phi_1 - \cos 2\phi_2) + 0.96(\cos 2\phi_1)(\cos 2\phi_2) + 1.15(\sin 2\phi_1)(\sin 2\phi_2)$. [c] There is another rotational barrier at $\phi_1 = 0°$. It is 2.0, 1.5, and 1.4 kcal mol^{-1} for NBANO, NBA, and PB, respectively. [d] Values given by RHF/6-31G** calculations.

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In the case of the liquid crystals with the nonplanar cores of NBANO, NBA, and PB types, the order in the clearing point is as follows:

$$\text{NBANO} > \text{NBA} > \text{PB}$$

The ΔT(—CH═N(O)—) of NBANO is greater than the ΔT(—CH═N—) of NBA. The difference is almost the same as [ΔT(—N(O)═N—) − ΔT(—N═N—)]. That is, the clearing point increases by about 20 °C in both cases, where the nitrogen atom in the core coordinates to the oxygen atom. The effect of the coordinated oxygen on the clearing point is so large that the clearing point of the liquid crystals with the core of nonplanar NBANO type is higher than that of the liquid crystal with the core of planar *t*-AB type, as shown in the figure.

The lowest position for PB is considered to be due to the following reasons. One is the difference in the dihedral angle, ϕ_1, of the phenyl ring. That is, the dihedral angle of the phenyl ring bonded to the oxygen atom of PB, $64^{+26}_{-12}\,^\circ$, is larger than that of the phenyl ring bonded to the nitrogen atom of NBA, 52(5)°,[23] at the 90% confidence level. The other is the difference in the barrier for the internal rotation of the phenyl ring. Among the barriers listed in Table 5, the barrier of the phenyl ring bonded to the oxygen atom of PB is somewhat lower than the others. Therefore, this phenyl ring is considered to perform a torsional motion with very large amplitude. Because the torsional angle of the phenyl ring is one of the factors determining the clearing point, it is reasonable to consider that the large-amplitude motion of the phenyl ring lowers the clearing point.

In conclusion, a noticeable relationship is found between the gas-phase structures of model compounds and T_{NI}. The following factors affect T_{NI}: (a) nonplanarity of cores; (b) large-amplitude motion of phenyl rings; (c) length of linking units; and (d) additional intermolecular interactions due to atomic charge of the coordinated oxygen atom.

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Supporting Information Available: Tables of the leveled total intensities and the backgrounds, the optimized geometrical parameters of the stable and pseudoconformers, the local symmetry coordinates, the force constants, the observed and calculated frequencies with potential energy distributions, the interatomic distances and mean amplitudes, the correlation matrix, and the experimental and theoretical molecular scattering intensities (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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