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Dynamics of Complex Phthalate Liquids. 1. Structural Effects of Molecular Framework

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The motional behavior of complex phthalates and structurally related liquids has been investigated in order to study the structural effect of molecular framework on the macroscopic and microscopic dynamic properties. ^{13}C NMR spin−lattice relaxation times and nuclear Overhauser enhancements (NOE) of individual carbon nuclei of bis(2-ethylhexyl) cyclohexane-1,2-dicarboxylate (DEHHP), bis(2-ethylhexyl) isophthalate (DEHIP), bis(2-ethylhexyl) terephthalate (DEHTP), and tris(2-ethylhexyl) trimellitate (TOTM) have been measured as a function of temperature from −40 to 90 °C. Individual ^{13}C peaks were unambiguously assigned by using 2D hydrogen−carbon chemical shift correlation spectra. In addition, the density and viscosity of these compounds as a function of temperature have been measured. The results were also compared with those of 2-ethylhexyl benzoate (EHB), 2-ethylhexyl cyclohexanecarboxylate (EHC), and bis(2-ethylhexyl) phthalate (DEHP), complex liquids studied earlier in our laboratory. Both the macroscopic and microscopic dynamic properties were significantly affected by the structure of the molecular framework. The conjugation between a phenyl ring and carboxyl groups was found to make the structural framework stiffer and resulted in an enhanced viscosity. The ^{13}C NMR relaxation data were interpreted in terms of a theoretical model assuming a Cole−Davidson distribution of correlation times. The internal motions of the common 2-ethylhexyl side chains were found to be independent of the nature of the molecular framework of the compounds. The parameter β in the Cole−Davidson model, representing the distribution width of the involved correlation times of the molecular motions, contained useful information on the detailed motional features of individual carbon nuclei. The β values for the rigid phenyl ring carbons reflected the reorientational anisotropy resulting from the molecular shape of the structural framework and could be successfully correlated with the parameter κ introduced by McClung and Kivelson in the modified Stokes−Einstein−Debye (SED) equation. On the other hand, the β values for the flexible cyclohexane ring carbons were affected by both the internal motion of the cyclohexane ring and the anisotropy of the molecular reorientation.

Introduction

The structure−property relationship for complex liquids is important from both basic and technological points of view. In tribological applications,[1] for example, the key factors determining the quality of the lubricants are affected by the chemical structure.[2] Therefore, the question of the effect of structural variations on the physical and chemical properties of liquids has attracted considerable attention in the hope of improving the performance characteristics of the functional fluids through modification of the chemical structure.[2−5]

In previous papers, we have discussed the NMR relaxation behavior of 2-ethylhexyl benzoate (EHB),[6,7] 2-ethylhexyl cyclohexanecarboxylate (EHC),[6,7] and bis(2-ethylhexyl) phthalate (DEHP).[8] Selection of these compounds was based on our continued efforts of studying the motional dynamics of complex, viscous (η > 1 P) fluids, which have been motivated by the need for improved understanding of the relationship between the microscopic molecular properties and the macroscopic bulk fluid properties of elastohydrodynamic lubricants. In the most recent study,[8] the motional behavior of DEHP was described in detail and compared with that of the monoester analogue (EHB). It showed that the motional behavior of DEHP is significantly different from EHB due to the structural change by the introduction of an additional ester side chain.

Realizing the importance of the relationship between the molecular structure of a complex liquid and its fluid properties led to the present study, which investigates the effect of the structural change on the physical and dynamic properties of complex liquids. On the basis of the results of our earlier studies, we have chosen several complex liquids with a molecular structure related to DEHP: bis(2-ethylhexyl) cyclohexane-1,2-dicarboxylate (DEHHP), bis(2-ethylhexyl) isophthalate (DEHIP), bis(2-ethylhexyl) terephthalate (DEHTP), and tris(2-ethylhexyl) trimellitate (TOTM). The structural formulas of these compounds are shown in Figure 1 along with the molecular structures of EHB, EHC, and DEHP. These molecules comprise industrially important fluids, with some used as general-purpose plasticizers or synthetic lubricants. All of the liquids studied have 2-ethylhexyl ester chain(s) in common, so the effect of structural modification in the molecular framework of the phthalates can be investigated.[9] These liquids can be grouped in several ways. For example, by comparing the properties of EHB and DEHP with those of EHC and DEHHP, the effect of replacing the rigid phenyl ring with a flexible cyclohexane ring can be studied. By comparing EHB, DEHP, and TOTM, and also EHC and DEHHP, the effect of the number of attached substituents can be examined. Comparison of the three structural isomers, DEHP, DEHIP, and DEHTP, allows one to estimate the effect of the relative position of the substituents in the phthalates.

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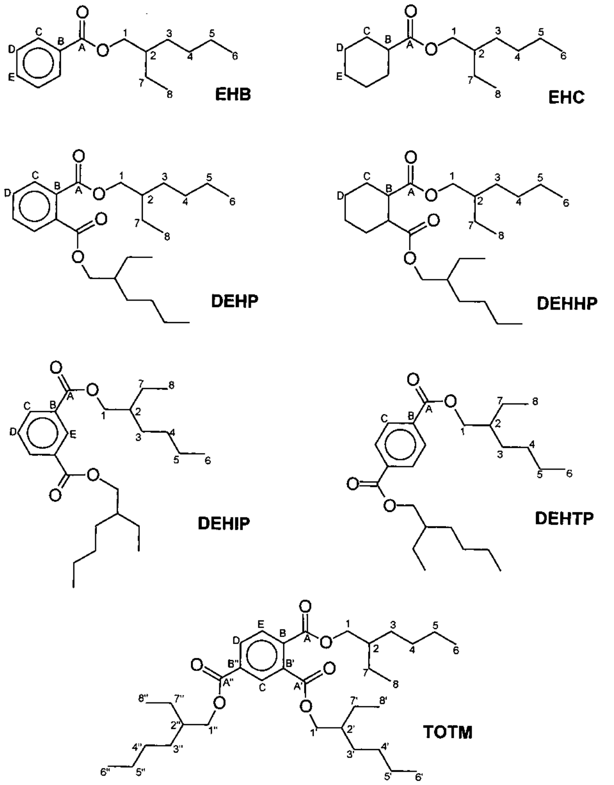

Figure 1. Structural formulas of the compounds studied. All carbon atoms are labeled considering chemical equivalence.

It is well-known that ^{13}C NMR relaxation experiments provide a wealth of information on the motional dynamics in complex fluids.[3,10−14] Combined with the fact that carbon atoms form a skeleton of most organic compounds, the good spectral dispersion of individual ^{13}C nuclei offers the advantage of probing the detailed motional features for different sites of the molecules. The relaxation of a ^{13}C nucleus is related to molecular motion via the spectral density function, $J(\omega)$, which is the Fourier transform of a correlation function describing the reorientational motion of a C−H internuclear vector. For carbon-13 nuclei relaxed by intramolecular dipolar interactions with attached protons, spin−lattice relaxation time (T_1) and nuclear Overhauser enhancement (NOE) are respectively expressed in terms of $J(\omega)$ by

$$\frac{1}{T_1} = \frac{N}{10}\frac{\gamma_C^{2}\gamma_H^{2}\hbar^{2}}{r_{CH}^{6}}[J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)] \tag{1}$$

$$\mathrm{NOE} = 1 + \frac{\gamma_H}{\gamma_C}\frac{6J(\omega_H + \omega_C) - J(\omega_H - \omega_C)}{J(\omega_H - \omega_C) + 3J(\omega_C) + 6J(\omega_H + \omega_C)} \tag{2}$$

where N is the number of directly attached protons, r_{CH} is the carbon−hydrogen bond length, ω_H and ω_C are the Larmor frequencies, and γ_H and γ_C are the magnetogyric ratios of ^{1}H and ^{13}C, respectively. The particular form of $J(\omega)$ depends on the model for molecular reorientation. In the previous study,[8] several theoretical models were tested for applicability to the motional behavior of a complex liquid, DEHP. Among them, the theoretical model assuming a Cole−Davidson distribution of correlation times proved to be the most suitable for describing the dynamic structure of the complex phthalate liquid. This model has successfully described the reorientational motions in many complex, viscous fluids.[7,8,14−16] In the Cole−Davidson distribution model,[17,18] the spectral density function assumes a distribution of isotropic reorientational correlation times given by

$$J(\omega) = \int_0^{\infty} \frac{g(\tau)\cdot\tau}{1 + \omega^2\tau^2}\,\mathrm{d}\tau \tag{3}$$

where the normalized probability density of the distribution, $g(\tau)$, takes the form

$$g(\tau) = \left[\frac{\sin(\beta\pi)}{\tau_0\beta\pi}\right]\left(\frac{\tau}{\tau_0 - \tau}\right)^{\beta} \qquad \text{for } 0 \le \tau_0 < \tau$$

$$= 0 \qquad \text{for } \tau_0 \le \tau \tag{4}$$

β is the distribution width and may assume a value from 0 to 1. In the case where $\beta = 1$, only one correlation time exists, and consequently the spectral density function reduces to that of the isotropic reorientational model. The distribution becomes wider as β approaches 0, and in the extreme limit of $\beta = 0$, an infinite number of correlation times are assumed. The average correlation time is $\bar{\tau} = \beta\tau_0$, and the spectral density function is

$$J(\omega) = \sin[\beta\,\arctan(\omega\tau_0)]/\omega[1 + (\omega\tau_0)^2]^{\beta/2} \tag{5}$$

The microscopic motional behavior usually characterized by reorientational correlation times can be related to the macroscopic viscosity of the fluids using the hydrodynamic Stokes−Einstein−Debye (SED) equation.[19−21] The SED equation has been used to describe the molecular motion of a particle immersed in a uniform fluid under the “stick” boundary conditions. In cases of nonideal conditions, due to the deviations from the assumed sphericity, boundary condition, and uniformity of surrounding medium, the hydrodynamic theory is not able to adequately predict the microscopic correlation times obtained experimentally. Introduction of the “slip” boundary conditions has greatly improved agreement between the hydrodynamic theory and experimental results.[23,24] A direct consequence of applying these conditions is that the reorientational correlation time for a sphere rotating under perfect slip conditions would have no viscosity dependence. As the molecule becomes less spherical, the viscosity dependence of the reorientational correlation time would be greater because of drag by solvent displacement, even in the slip limit.[25] The success of the slip boundary conditions in explaining the experimental data in many liquids implies the importance of molecular shape in determining the viscosity dependence of reorientation.[26]

The concept of coupling between the molecular rotation and the translational motions in liquids is explicitly expressed in the modification by McClung and Kivelson.[27] In the modified SED equation, the functional dependence of the reorientational correlation times, τ_θ, upon viscosity is given by

$$\tau_\theta = \kappa V_H\eta/kT + \tau_H \tag{6}$$

where V_H is the hydrodynamic volume, τ_H is the zero viscosity correlation time similar to the free rotor correlation time,[28] and η is the shear viscosity. The McClung and Kivelson constant, κ, represents the ratio of the mean square intermolecular torques on the solute molecules to the mean square intermolecular forces on the solvent molecules, reflecting the extent of the coupling between the rotational and the translational motions. Consequently, κ provides information about the degree of motional anisotropy. The validity of eq 6 has been justified in several complex, viscous liquids including EHB and EHC,[6,29] although the degree of rotational−translational coupling appeared to be affected by temperature or pressure if applied over an extended range of viscosity.[15,26,30] In all cases, the molecular shape has a significant effect on the rotational−translational coupling in neat liquids.[3,26,30−33]

As already mentioned, the main purpose of this study is to investigate the effect of the structural change on the macroscopic and microscopic properties of complex liquids including lubricants. In the present experiment, natural-abundance ^{13}C spin−lattice relaxation times (T_1) and NOEs of individual carbons in DEHHP, DEHTP, DEHIP, and TOTM have been measured as a function of temperature from −40 to 90 °C. In addition, density and viscosity for these liquids have been measured in a similar temperature range. By comparing the microscopic motional behavior and the macroscopic viscosity of these compounds including EHB, EHC, and DEHP, the effects of structural variation on these important properties can be discussed. The SED equation offers another opportunity to relate these macroscopic and microscopic quantities obtained experimentally and to provide information about the effect of molecular framework of phthalate liquids on their motional behavior via the parameter κ (eq 6).

Experimental Section

The samples were purchased and used without further purification: DEHHP (98%+, Chem Service), DEHTP (98.5%+, Eastman), DEHIP (98%+, Chem Service), and TOTM (99%+, Aldrich). The densities were measured at various temperatures with a commercial Anton Paar DMA 45 digital density meter. The measuring principle of this instrument is based on the change in the natural vibration frequency of a hollow oscillator when filled with fluids of different densities. The maximum error is estimated to be 2.0 × 10^{-4} g/cm^3.

Kinematic viscosity measurements were made by using a calibrated Cannon-Fenske glass capillary viscometer. The viscometer was placed in a transparent liquid of which the temperature was controlled by a thermostat. Below 0 °C the measurement setup was isolated from the atmosphere in order to avoid moisture condensation. The accuracy of the viscosity measurements is estimated as ±2%. The resultant kinematic viscosity data were converted to dynamic viscosity using the measured density data interpolated to the same temperature.

Carbon-13 NMR relaxation measurements were performed at 45.2 or 100.6 MHz. The home-built NMR spectrometer system with a 4.2 T magnet (for the relaxation measurements at 45.2 MHz) as well as the techniques of relaxation measurements have been described in the previous report.[8] The relaxation measurements at 100.6 MHz and the two-dimensional ^{1}H−^{13}C correlation (HETCOR) spectra for the carbon-13 peak assignments were taken using a Varian Unity 400 FT spectrometer in the VOICE NMR Laboratory, School of Chemical Sciences, University of Illinois. The temperature of the Unity 400 spectrometer was controlled by a VT unit which used the flow of temperature-regulated nitrogen gas. The temperature was calibrated using chemical shift differences in ethylene glycol and methanol samples for high and low temperature, respectively.[34,35]

All the NMR samples were degassed by the freeze−pump−thaw method before the relaxation measurements. The measured T_1 and NOE values were reproducible within the error of ±5% and ±10%, respectively.

Results and Discussion

(A) ^{13}C Peak Assignments. The identification of each peak is a prerequisite for probing the motional behavior in these complex liquids by observing the relaxation behavior of individual carbon nuclei. All carbon-13 nuclei of DEHHP, DEHTP, DEHIP, and TOTM were well resolved in the NMR spectra for the relaxation measurements under the experimental conditions, except for carbon nuclei D and 7 of DEHHP, which overlap accidentally. In TOTM, the corresponding alkyl carbons in the three ester chains (e.g., 1, 1′, and 1″) are not chemically equivalent and have slightly different ^{13}C chemical shifts. However, the relaxation data for the three corresponding carbon nuclei were almost the same, and an average value was used in the analysis as representing the set of the corresponding carbons.

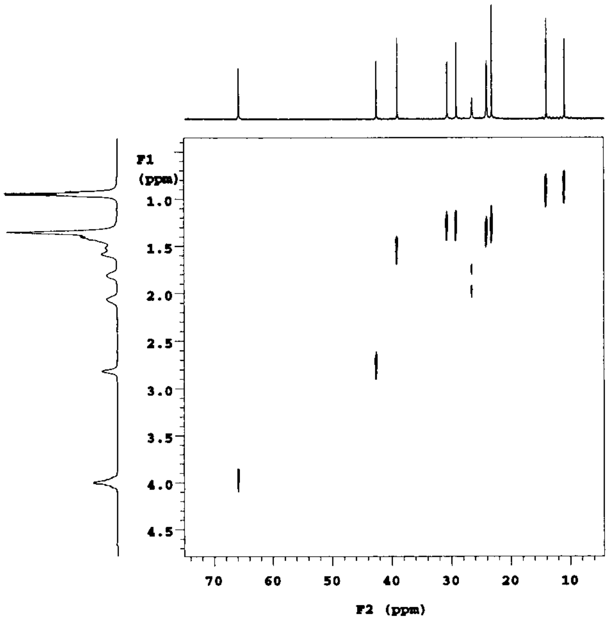

Figure 2. 2D HETCOR of DEHHP at 298 K. The vertical axis (F1) and the horizontal axis (F2) represent ^{1}H and ^{13}C chemical shifts, respectively.

All the carbon-13 spectral peaks were unambiguously assigned with the aid of 2D HETCOR spectra. Figure 2 shows the 2D HETCOR spectrum of DEHHP. The peaks for D and 7 in the ^{13}C dimension (24.1 ppm on the F2 axis) were not resolved, even in the high magnetic field of 9.3 T. The two diastereotopic protons attached to carbon C appear as two distinct peaks in the ^{1}H dimension (1.77 and 2.02 ppm on the F1 axis) and are clearly correlated to the signal of the C carbon nuclei (26.6 ppm in F2 dimension). There are two possible stereoisomers for the structure of DEHHP, cis and trans, according to the relative configuration of the two ester substituents. It is known[36−39] that *cis*-1,2-cyclohexanedicarboxylic ester is a flexible molecule undergoing inversion of the cyclohexane ring with frequent interconversion of its axial and equatorial ester groups, while the trans isomer is relatively rigid in its "exclusively" preferred diequatorial conformation. Although information on the stereoisomerism of the commercial DEHHP sample was not available, the ^{13}C chemical shifts of the carbonyl carbon (A) and cyclohexane ring carbons (B−D)[39] as well as ^{1}H chemical shift data[40] indicate the cis isomer. The complete chemical shift assignments for ^{13}C of the compounds including EHB,[6] EHC,[6] and DEHP[8] relative to tetramethylsilane (TMS) are given in Table 1. The chemical shifts for the alkyl carbons (1−8) in the common 2-ethylhexyl ester chains are practically the same for all of the liquids studied.

(B) Density and Viscosity Measurements. Density and viscosity are fundamental bulk properties of liquids. In fact, viscosity and its temperature dependence represents critical bulk property in determining the lubricant performance. Despite the

TABLE 1: Carbon-13 Chemical Shift Assignments for the Compounds Studied (Chemical Shifts (ppm) Are Relative to TMS)

carbon[a]	EHB[b]	EHC[b]	DEHP[c]	DEHHP	DEHIP	DEHTP	TOTM
A			167.0	172.4	164.9	164.7	166.4, 165.8, 164.2
B	130.8	43.1	133.0	42.7	131.3	134.2	137.0, 132.8, 132.6
C	128.1	29.2	129.0	26.7	133.6	129.3	129.99
D	129.6	25.6	130.9	24.2	128.6		131.90
E	132.4	26.1			130.6		129.08
1	66.6	65.8	67.6	66.0	67.2	67.1	67.77, 67.68, 67.44
2	39.0	39.3	39.1	39.2	39.2	39.0	39.12, 39.05, 38.96
3	30.6	30.2	30.7	30.8	30.9	30.7	30.76, 30.67, 30.60
4	29.0	29.2	29.2	29.3	29.3	29.1	29.18, 29.14
5	23.0	23.1	23.2	23.3	23.3	23.1	23.20, 23.17
6	13.9	13.8	14.2	14.2	14.2	14.0	14.09, 14.06
7	24.0	24.1	24.0	24.2	24.3	24.1	24.16, 24.04, 23.96
8	10.9	10.9	11.1	11.1	11.2	11.0	11.06, 11.03, 10.98

[a] See Figure 1 for the carbon nuclei labels. [b] The assignments are from ref 6. [c] The assignments are from ref 8.

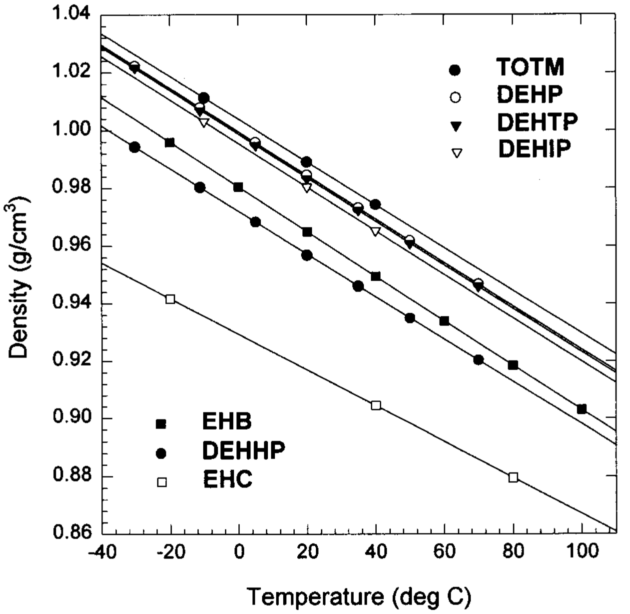

Figure 3. Densities of the liquids studied as a function of temperature. The data for EHB and EHC are from refs 29 and 6, respectively. The densities of DEHP have been reported in the literature,[41] and they agree well with the experimental data.

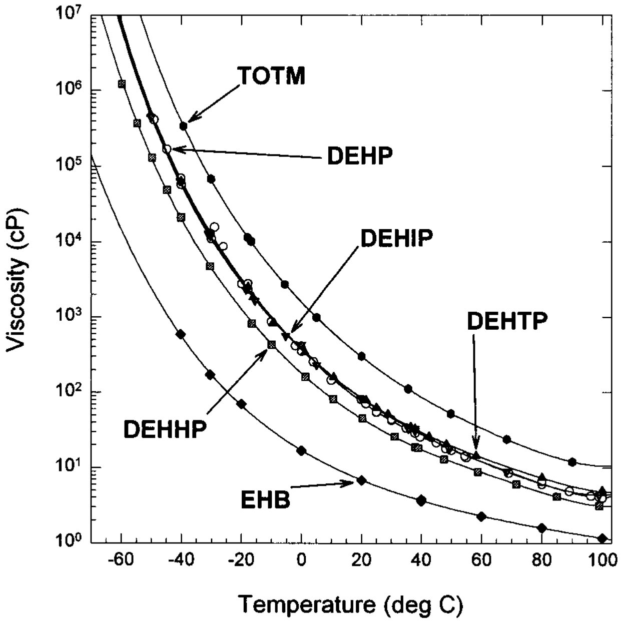

Figure 4. Viscosities of the liquids studied as a function of temperature. The data for EHB are from ref 29. Some of the data points for DEHP are from the literature.[42] The viscosity of EHC[6] is not shown here.

wide applications of these complex liquids as functional fluids, reliable data over the proper working range for this important physical properties have not been reported. The temperature dependencies of the density of the liquids are shown in Figure 3, where the densities of all the liquids are very well represented as a linear function of temperature. Also the temperature coefficients of density of these liquids are nearly the same ($(7.5 \pm 0.1) \times 10^{-4}$) except for EHC. The density of the liquids with a cyclohexane ring (EHC and DEHHP) is lower than that of the analogues with a phenyl ring (EHB and DEHP) over the entire temperature range of the measurements. This trend is understandable if one compares the planar and relatively rigid structure of the aromatic ring with the more bulky three-dimensional nature of the cyclohexane ring, which makes the effective molecular volume of EHC and DEHHP larger. The densities of the three structural isomers (DEHP, DEHIP, and DEHTP) were found to be similar.

The viscosities of the liquids studied as a function of temperature are shown in Figure 4. The temperature dependence of the viscosity of all the liquids is well described by the Vogel−Fulcher−Tammann (VFT) equation.[43] As shown in the Figure 4, the greater number of ester side chains that are attached to a molecule, the higher the viscosity of the liquid (TOTM $>$ DEHP $\cong$ DEHTP $\cong$ DEHIP $>$ EHB, and DEHHP $>$ EHC). On the basis of the observation that the temperature−viscosity dependencies of the three isomers are very similar, the relative position of the substituents in these structures is not considered to affect significantly the bulk liquid viscosity.

It is interesting to compare the viscosity of the compounds with a planar aromatic ring to their counterparts with a cyclohexane ring. It is a general trend that the viscosity of the hydrocarbon fluids with a cyclohexane ring is higher than that of phenyl analogues.[4,44,45] In an earlier report,[6] a different trend was observed and the higher viscosity of EHB over EHC was attributed to the possible conjugation of the phenyl group with the ester group in EHB. The effect of conjugation on the viscosity is very evident in the present study when one compares the viscosity of these two series of liquids with different numbers of substituents, which is shown in Figure 5. As the number of conjugated substituents attached to an aromatic phenyl ring increases, the increment of viscosity is greater than the viscosity increment in a cyclohexane ring accompanied with the addition of the same, but nonconjugated, substituents. With the conjugation, the rotation of the C−C bonds between the phenyl and the carboxyl group is hindered due to the delocalization of the electronic density around the conjugated double bonds. As a result, the molecular structure becomes stiffer, which is manifested macroscopically in an increased viscosity.

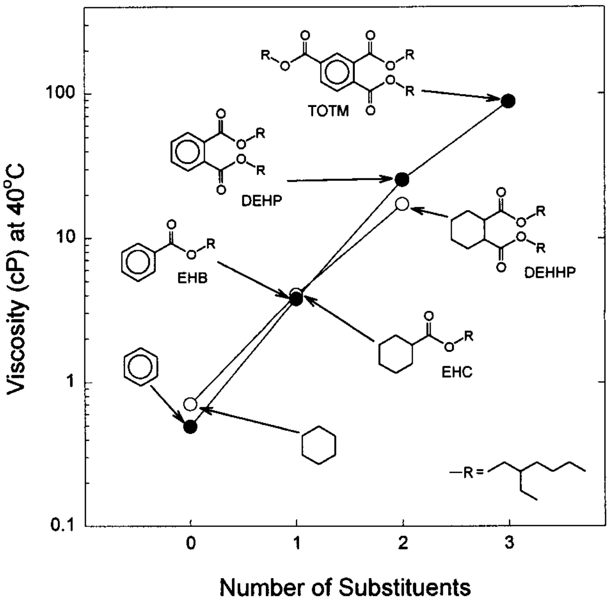

Figure 5. Effect of conjugation in molecular structure on viscosity. Solid circles represent the viscosity of the series of compounds with an aromatic ring at 40 °C. The carboxyl groups in these liquids are considered to be conjugated with the phenyl ring. Open circles represent the viscosity of the series of compounds with a cyclohexane ring at the same temperature.

(C) ^{13}C NMR Relaxation Data Analysis. The experimental T_1 data of the carbon nuclei in DEHHP, DEHTP, DEHIP, and TOTM as a function of temperature are shown in Tables 2–5. The spin–lattice relaxation times for DEHHP and DEHTP in Tables 2 and 3 were measured at 45.2 MHz, and the data for DEHIP and TOTM shown in Tables 4 and 5 were measured at 100.6 MHz. These data are included to help stimulate theoretical efforts aimed at improving the understanding of the motional dynamics of complex liquids. The low-temperature limit of the T_1 measurements for each carbon was determined by a low signal-to-noise ratio or inability to resolve the individual peak at that temperature. The carbon nuclei without any attached protons (A and B) are considered to be relaxed by mechanisms other than intramolecular dipolar interactions and are not analyzed here. For the methyl carbons (6 and 8), the application of the Cole–Davidson distribution model with the dipolar relaxation formalism is limited by the extremely broad distribution of correlation times arising from rapid internal rotation about the C_3 symmetry axis and the concurrent contribution of the spin–rotation (SR) relaxation mechanism.

The experimental relaxation data for the individual carbon nuclei were analyzed in terms of a model assuming a Cole–Davidson distribution of relaxation times. The detailed method of analysis has been described previously.[8] In short, the theoretical expressions for T_1 and NOE, eqs 1 and 2, with $J(\omega)$ replaced by the spectral density function of the Cole–Davidson distribution model, eq 5, were fitted to the experimental data to yield a set of optimum parameters. Analysis of the relaxation data as a function of temperature requires an expression for the relationship between temperature and correlation time, τ. The limiting correlation time τ_0 in the Cole–Davidson distribution model was assumed to have a VFT temperature dependence:

$$\tau_0 = \tau_0^* \exp\left(\frac{B}{T - T_0}\right) \tag{7}$$

where τ_0^*, B, and T_0 are constants. T_0 is the temperature at which both the correlation time for the overall motions and the viscosity would be infinite. T_0 for each compound was determined by fitting the temperature-dependent viscosity data (Figure 4) to a VFT equation of

$$\eta = \eta^* \exp(B_\eta/(T - T_0)) \tag{8}$$

where η^* and B_η are constants.

Thus, the fitting equation contained three adjustable parameters: τ_0^* (the preexponential factor for the limiting correlation time), B (the temperature coefficient in the VFT equation), and β (the distribution width). All these parameters were assumed

TABLE 2: Temperature Dependence of ^{13}C Spin–Lattice Relaxation Times (seconds) of the Individual Nuclei of DEHHP Measured at 45.2 MHz

carbon[a]	70 °C	50 °C	30 °C	20 °C	10 °C	0 °C	−10 °C	−20 °C	−30 °C
A	5.66	3.38	1.92	1.44	1.20	1.31	2.31		
B	0.429	0.244	0.147	0.120	0.104	0.110	0.185	0.425	
C	0.214	0.123	0.0751	0.0605	0.0568	0.0594	0.0988		
1	0.383	0.217	0.121	0.0916	0.0740	0.0672	0.0856	0.111	
2	0.694	0.384	0.208	0.159	0.129	0.115	0.142	0.221	
3	0.696	0.384	0.205	0.152	0.116	0.0943	0.0942	0.116	
4	1.14	0.634	0.334	0.240	0.178	0.139	0.127	0.138	
5	1.95	1.12	0.584	0.413	0.295	0.215	0.170	0.163	0.185
6	3.99	2.76	1.69	1.26	0.955	0.720	0.537	0.456	0.418
8	2.71	1.79	1.11	0.835	0.652	0.520	0.432	0.406	0.384

[a] The carbon peaks for D and 7 were not resolved from each other for the measurements.

TABLE 3: Temperature Dependence of ^{13}C Spin–Lattice Relaxation Times (seconds) of the Individual Nuclei of DEHTP Measured at 45.2 MHz

carbon	70 °C	50 °C	30 °C	20 °C	10 °C	0 °C	−11 °C	−21 °C
A	4.64	2.88	1.95	1.90	2.22	2.98	4.79	
B	3.58	2.12	1.38	1.28	1.40	1.85	3.38	
C	0.300	0.181	0.120	0.104	0.108	0.148	0.257	
1	0.204	0.133	0.0872	0.0738	0.0727	0.0774	0.107	0.143
2	0.394	0.235	0.153	0.130	0.122	0.138	0.198	0.335
3	0.452	0.258	0.158	0.126	0.104	0.101	0.119	0.142
4	0.829	0.456	0.259	0.203	0.156	0.143	0.145	0.160
7	0.471	0.273	0.166	0.133	0.108	0.103	0.121	
5	1.49	0.808	0.458	0.344	0.257	0.209	0.185	0.189
6	3.23	2.30	1.42	1.14	0.850	0.664	0.571	0.468
8	2.13	1.45	0.930	0.782	0.606	0.512	0.479	0.421

TABLE 4: Temperature Dependence of ^{13}C Spin−Lattice Relaxation Times (seconds) for the Proton-Bearing Carbon Nuclei of DEHIP Measured at 100.6 MHz

carbon	91.3 °C	74.0 °C	58.0 °C	44.4 °C	36.8 °C	29.5 °C	19.9 °C	10.6 °C	−0.7 °C	−15.1 °C
C	0.352	0.260	0.203	0.175	0.172	0.179	0.218	0.315	0.523	1.30
D	0.491	0.344	0.249	0.204	0.187	0.183	0.208	0.270	0.454	1.05
E	0.477	0.330	0.247	0.196	0.187	0.188	0.204	0.274	0.463	
1	0.475	0.341	0.244	0.188	0.169	0.160	0.158	0.173	0.203	0.315
2	0.870	0.610	0.446	0.337	0.303	0.278	0.270	0.299	0.365	0.574
3	0.931	0.620	0.431	0.323	0.282	0.252	0.223	0.216	0.223	0.262
4	1.67	1.07	0.732	0.537	0.451	0.392	0.335	0.302	0.287	0.312
7	0.967	0.645	0.449	0.337	0.291	0.260	0.233	0.224	0.224	0.260
5	2.87	1.92	1.29	0.924	0.765	0.636	0.531	0.454	0.387	0.363
6	5.61	4.15	3.11	2.37	1.94	1.70	1.43	1.22	0.948	0.762
8	3.93	2.90	2.18	1.66	1.43	1.23	1.07	0.942	0.803	0.692

TABLE 5: Temperature Dependence of ^{13}C Spin−Lattice Relaxation Times (seconds) for the Proton-Bearing Carbon Nuclei of TOTM Measured at 100.6 MHz

carbon	91.3 °C	74.0 °C	58.0 °C	44.4 °C	29.5 °C	19.9 °C	10.6 °C	−0.7 °C	−10.4 °C
C	0.224	0.182	0.178	0.210	0.330	0.450	0.719		
D	0.207	0.175	0.171	0.214	0.345	0.499	0.859		
E	0.226	0.184	0.172	0.206	0.315	0.477	0.744		
1	0.277	0.207	0.179	0.165	0.175	0.203	0.240	0.312	0.412
2[a]	0.526	0.388	0.312	0.288	0.301	0.341	0.405	0.539	0.704
3[a]	0.586	0.406	0.310	0.258	0.230	0.229	0.237	0.265	0.290
4[a]	1.06	0.711	0.527	0.412	0.344	0.318	0.319	0.329	0.345
7[a]	0.620	0.427	0.323	0.269	0.235	0.232	0.236	0.264	0.301
5[a]	1.97	1.35	0.916	0.702	0.539	0.476	0.443	0.420	0.409
6[a]	4.65	3.43	2.63	1.97	1.52	1.29	1.12	0.958	0.828
8[a]	3.11	2.24	1.78	1.42	1.14	1.02	0.924	0.830	0.759

[a] The corresponding alkyl carbons (e.g., 1, 1′, and 1″) in the three ester chains of the TOTM molecule are not chemically equivalent and have different ^{13}C chemical shifts, although they are very close. The T_1 values for these corresponding carbons are almost the same, and the T_1's reported here are the average for the three corresponding peaks.

to be temperature-independent. The justification of this assumption for β was based[8] on the fact that the T_1 values at its minimum did not vary much at different temperatures and pressures if the frequencies of the relaxation measurements were the same. As expected from their structural similarity with DEHP, the experimental relaxation data for DEHHP, DEHTP, DEHIP, and TOTM were very well represented by the Cole−Davidson distribution model. The optimized set of parameters of this model simultaneously represented the experimental T_1 and NOE data. As an illustration of the quality of the fits, the $N{\cdot}T_1$'s plotted as a function of temperature for the individual carbon-13 nuclei in DEHHP and TOTM using the Cole−Davidson distribution model are shown in Figure 6a,b, respectively. Similar fits were obtained for the experimental data of the remaining complex liquids.

Information on the motional behavior of these molecules can be obtained from the interpretation of the optimized parameters of the Cole−Davidson distribution model. As discussed in the previous paper,[8] τ_0* and B, among three parameters, are considered to describe the motional behavior as a whole (the overall motion), and β contains information about the motional details of individual carbon nuclei from which the internal motion of the molecule can be estimated. The correlation time for the overall motion described by τ_0* and B via eq 7 are in fact the limiting correlation time of the Cole−Davidson model which represents the slowest process of the molecular motion that rotationally averages a particular C−H relaxation vector. From the optimized set of parameters, however, we found that the resultant limiting correlation times for the alkyl carbons decreased along the ester side chain away from the ring. This may be because the effect of the overall motion could decrease along the alkyl side chain due to the extensive segmental and internal motions. Hence it seems more appropriate that the correlation times for the overall motion are estimated from the τ_0* and B values of only the ring carbon atoms. The optimized τ_0* and B values averaged for the ring carbon atoms of the liquids are shown in Table 6.

TABLE 6: Optimized Parameter Values for Overall Motion (τ_0* and B) in the Cole−Davidson Distribution Model from the Fits of the Relaxation Data vs Temperature for the Ring Carbons in the Liquids Studied[a]

compound	τ_0*(293K) (ns)	B (K)
DEHHP	2.9	1503
DEHTP	5.5	1519
DEHIP	3.8	1326
TOTM	14.5	1469

[a] Instead of using eq 7, the τ_0* value was converted into the value at room temperature, τ_0*(293.15K), by $\tau_0 = \tau_0{*}(293.15\text{K})\exp[B/(T - T_0) - B/(293.15 - T_0)]$.

The parameter β, the distribution width, is an indication of the range of the frequency of motions involved in the reorientation of a particular C−H relaxation vector. The optimized values of β for individual carbon nuclei of the liquids with a rigid phenyl ring are shown in Figure 7. It is apparent by comparison that the β values of the 2-ethylhexyl side chain carbons are very similar in all of the liquids. This confirms that the internal motions of these flexible alkyl side chains are independent of the motional behavior of the relatively rigid ring part of the molecule and that they are not affected by the structural variation in the framework of the compounds.

In contrast to the similarity of β values in alkyl carbons, the β values for phenyl ring carbons in these compounds are quite different. Considering the rigidity of the phenyl ring, the large variance should result from the anisotropy of the reorientational motions of the molecules. In general,[25,46,47] the relaxation for a particular ^{13}C nucleus is governed by an effective correlation time, which is a weighted sum of three reorientational correlation times for rotations about the three principal axes of a molecule.

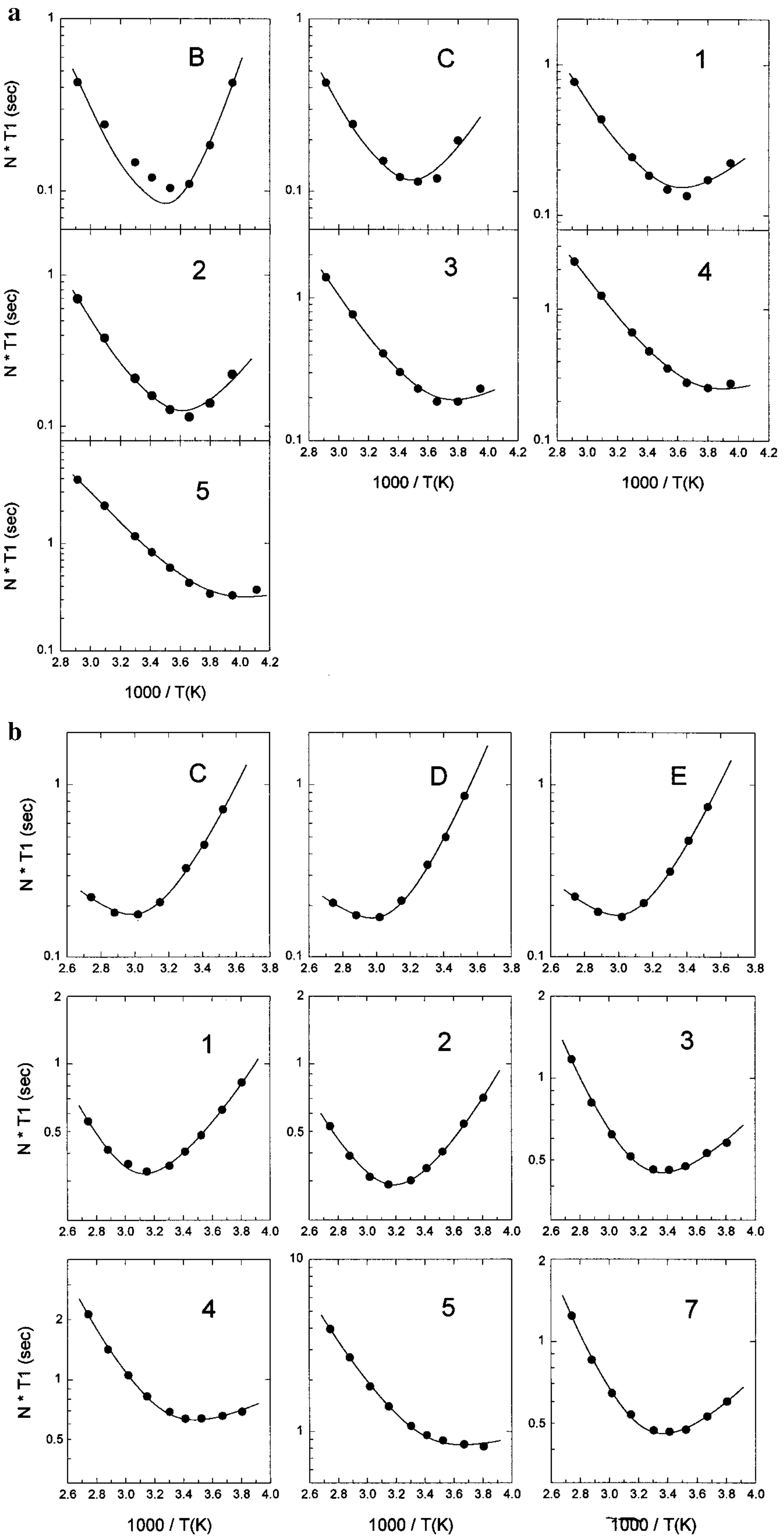

Figure 6. (a) The 45.2 MHz ^{13}C $N{\cdot}T_1$'s of DEHHP fitted by the Cole–Davidson distribution model. Solid circles indicate the experimental values, and the line represents the fitting results using the optimized parameters. For the carbon labels, refer to Figure 1. The ^{13}C peaks for D and 7 overlap and the relaxation times for these nuclei could not be measured. (b) The 100.6 MHz ^{13}C $N{\cdot}T_1$'s of TOTM fitted by the Cole–Davidson distribution model. Solid circles indicate the experimental values, and the line represents the fitting results using the optimized parameters. The experimental T_1 values for the alkyl carbons are averages for the corresponding carbons in the three ester chains.

The relative weights of these coefficients depend on the angle between the C–H relaxation vector and the principal axes. The wide distribution indicated by the lower values of β in the rigid framework can therefore be related to a large anisotropy in a

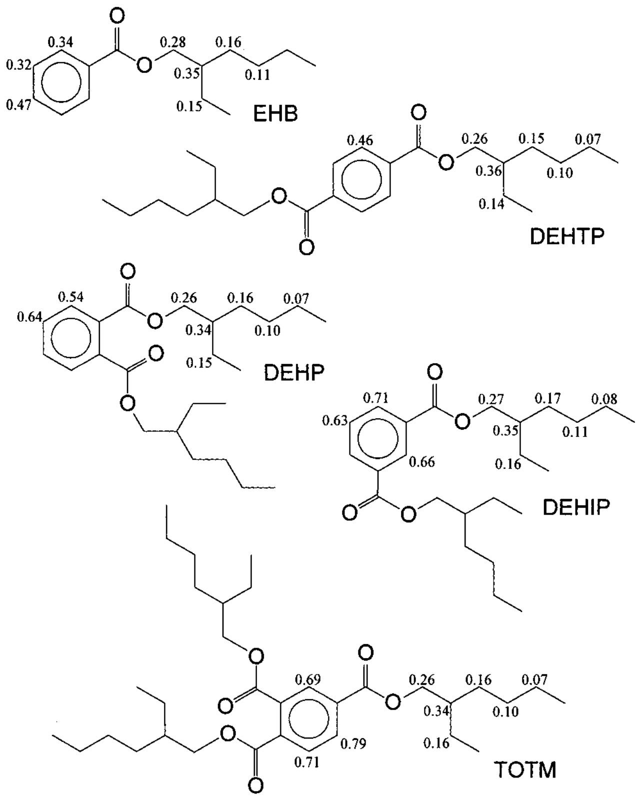

Figure 7. Comparison of the β values in the Cole–Davidson distribution model for the analyzed carbon nuclei in the compounds containing a rigid phenyl ring. The β values for EHB and DEHP are from refs 7 and 8, respectively.

molecule in which the correlation times about three principal axes differ greatly. If the relaxation vector of a ^{13}C nucleus coincides with the preferred axis of rotation of a molecule, the effective distribution width for this particular nuclei can be narrowed (β increased) because the contribution of the (smallest) correlation time for the preferred axis becomes negligible. The C–H relaxation vector parallel to the symmetry axis of a symmetric top is an example of this case. As the molecular motion of a molecule becomes isotropic, the β value becomes larger as it approaches the extreme case of $\beta = 1$ for the spherical top rotating isotropically. In this respect, the β values for the carbon atoms of a phenyl ring can be used to qualitatively estimate the characteristic reorientational motion and degree of anisotropy in compounds of different structure.

In the previous study,[8] the higher β value of carbon E in EHB (compared to carbons C and D) as well as carbon D in DEHP (compared to carbon C) was explained by the dominant reorientation along the axis that runs through carbon E in EHB and along the axis perpendicular to the D–D′ bond in DEHP, respectively. Judging by the difference in β values of ring carbons, similar anisotropy seems to exist for DEHIP and TOTM. However, the increased β values of the ring carbons in these two liquids compared with those of EHB or DEHTP indicate that the reorientational anisotropy is greatly reduced in TOTM and DEHIP by the presence of additional ester chains off the preferred axis of rotation. Information of this kind is not available for DEHTP in which all the proton-bearing carbons in the phenyl ring are chemically equivalent, although one can imagine quite large rotational anisotropy from the structure. By comparing the β values of the ring carbons, one can see that the rotational anisotropy is decreased in order EHB $\geq$ DEHTP $>$ DEHP $\geq$ DEHIP $>$ TOTM, which is not far from the expectation based on molecular structure.

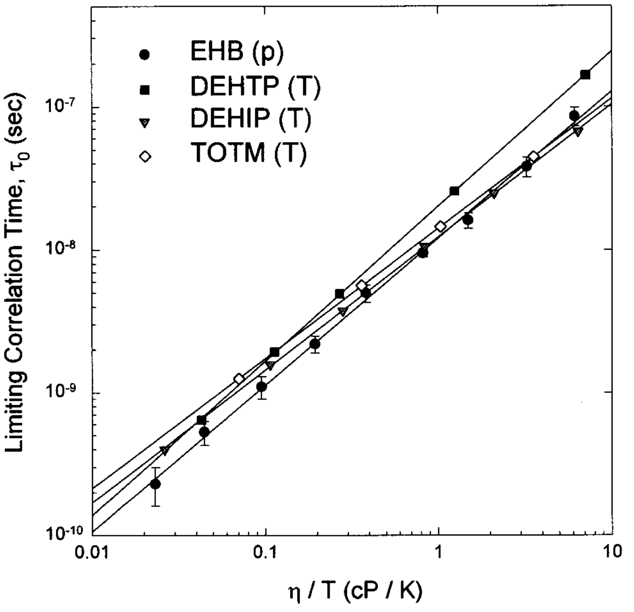

Figure 8. Plot of τ_0 in the Cole–Davidson model versus η/T for selected compounds. Both temperature-dependent (DEHTP, DEHIP, and TOTM) and pressure-dependent (EHB) viscosity and τ_0 values are used. For EHB, the NOE data are available only for E carbon nuclei.[7] For clarity, the plots for DEHP are not shown here. Pressure-dependent viscosity data for EHB and DEHP are from refs 29 and 48, respectively. The calculation of τ_0's are described in the text.

The notion that the parameter β in the Cole–Davidson model for the rigid structural unit can be used to describe the motional features characterized by the molecular shape stimulated us to correlate β with κ, the McClung and Kivelson constant in the modified SED equation,[27] eq 6. Reflecting the extent of coupling between the rotational and translational motions, κ provides information about the degree of anisotropy which characterizes molecular motions. In an earlier report,[26] Fury and Jonas could successfully correlate κ with the structural factors calculated from the molecular dimensions for small organic molecules. To estimate κ for these complex liquids, the reorientational correlation times (τ_0 in the Cole–Davidson model) were plotted versus η/T, which is shown in Figure 8. In this analysis, both temperature (for DEHP,[8] DEHTP, DEHIP, and TOTM) and pressure (for EHB[7] and DEHP[8]) were used as variables causing variation of viscosity (as well as τ_0). The reorientational correlation times from the temperature-dependent relaxation data were calculated by eq 7 using the optimized parameters shown in Table 6. For the pressure-dependent relaxation data, τ_0 was directly calculated[49] from T_1 and NOE data at each pressure without resorting to any relationship between pressure and correlation time. As is shown in Figure 8, the reorientational correlation times obtained from the Cole–Davidson distribution model are well correlated with η/T in the viscosity range extended to 10 000 cP.

Calculating κ from the slope of the τ_0 vs η/T plot requires knowledge of the hydrodynamic volume, V_H, or equivalently the hydrodynamic diameter. In general, the hydrodynamic diameter is approximated by the hard-sphere diameter (σ) in the rough hard-sphere (RHS) model[50] and can be determined from the experimental viscosity and density data for the simple liquid system. Unlike the case of simple molecular liquids, the procedures normally employed for the determination of σ could not be applied to these complex, viscous fluids for the following reasons. For most of the experimental conditions, the densities of the liquids studied were beyond the range of applicability of Chandler's expression[50,51] in the RHS model ($0.70 \leq \rho\sigma^3 \leq$

TABLE 7: van der Waals Volume (V_W) Estimated by Using Bondi's Method of Additive Molecular Group Increments[54,a]

compound	V_W (cm^3/mol)	V_M (cm^3/mol)	p
EHB	146.30	243.82	0.600
DEHP	246.76	398.23	0.620
DEHTP	246.76	398.59	0.619
DEHIP	246.76	399.86	0.617
TOTM	347.22	554.86	0.626

[a] The packing fraction (p) was obtained by dividing the molar volume (V_M) calculated from the density at 25 °C by V_W.

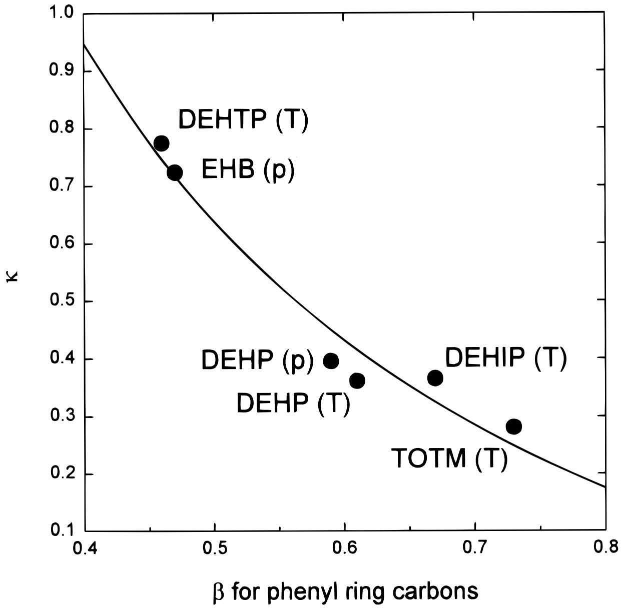

Figure 9. Correlation of β in the Cole–Davidson distribution model with κ in the modified SED equation for the compounds with a phenyl ring. β is the average value for the ring carbons in Figure 7, with the exception of EHB. κ's were determined from the slope of the lines in Figure 8.

0.97). Another method for obtaining σ based on the expressions proposed by Hildebrand and Lamoureaux[52] also failed because a plot of fluidity ϕ ($\phi = 1/\eta$) vs molar volume (V_M) for these complex liquids exhibited large curvature, which prevents the calculation of σ from the intercept of an extrapolated linear correlation between ϕ and V_M.[53] Therefore the hydrodynamic volume of these liquids was estimated using Bondi's method of additive molecular group increments[54] which, despite its approximate nature, provided impressive agreement with the values obtained by the fluidity analysis for EHB.[6] The molecular volumes (V_W) calculated by Bondi's method for these compounds are tabulated in Table 7, where they are compared with the molar volume calculated from the measured density data at 25 °C.

The correlation between β in the Cole–Davidson distribution model and κ in the modified SED equation is presented in Figure 9. The inverse correlation of β with κ for the rigid phenyl ring carbons, which is well represented in the figure, is physically understandable. For molecules with a small degree of anisotropy (higher β), the reorientation of the molecule does not necessitate much displacement of the neighboring molecules, resulting in a lowering of κ in the "slip" boundary conditions. For an ideal sphere ($\beta \sim 1$) rotating under perfect slip conditions, the reorientation time would have no viscosity dependence ($\kappa \sim 0$) and the sphere would rotate inertially.[25,55] As the molecular motion becomes more anisotropic (smaller β) due to the deviation of the molecular structure from a spherical shape, the tumbling motion of the molecule will displace more neighboring molecules and the correlation time for the reorientation is expected to be more sensitive to the viscosity of the medium (higher κ).

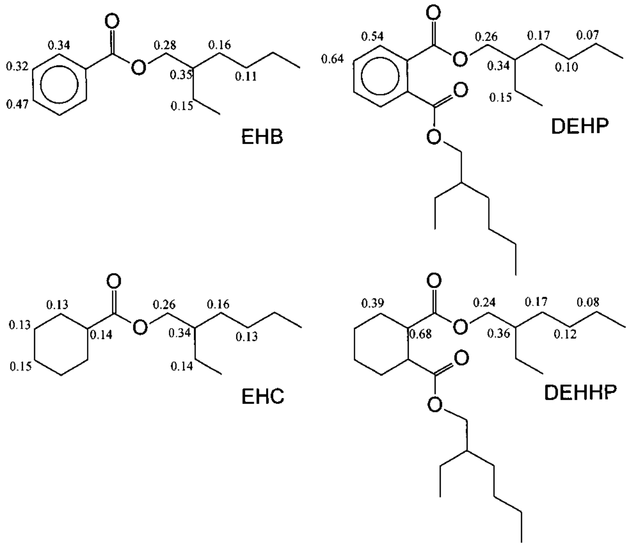

Figure 10. Comparison of the β values in the Cole–Davidson distribution model for the analyzed carbon nuclei in the molecules containing a rigid phenyl ring and a cyclohexane ring. The β values for EHC are from ref 7. The data for carbons D and 7 in DEHHP are not available due to spectral overlap.

The β values for compounds with a cyclohexane ring are compared with those of their analogues with a phenyl ring in Figure 10. Again, the β values of the alkyl carbons are very similar in all of the molecules, irrespective of the nature of the ring or the number of substituents. As for the ring carbons, the β values of the cyclohexane ring in EHC and DEHHP are smaller than those for the corresponding carbons of the phenyl ring in EHB and DEHP, reflecting the flexible nature of a cyclohexane moiety. The β values for carbon B in DEHHP (0.68) is unexpectedly high. The reliability of this value is somewhat doubtful, however, judging from the relatively poor fit for this ^{13}C nucleus in Figure 6a. The reason for this discrepancy of carbon B in DEHHP is not clear at present, although there is the possibility of contributions from other relaxation mechanisms.

Even with the uncertainty involved in the parameters for carbon B in DEHHP, the β values for the cyclohexane ring carbons in DEHHP are larger than what is expected from the flexible nature of the cis isomer. This is obvious when β values for EHC and DEHHP ring carbons are compared. As discussed above for the phenyl ring carbons, the relatively large β values of the DEHHP ring carbons may also be attributed to the molecular shape of DEHHP. We have employed molecular modeling combined with molecular mechanics calculations in order to gain some insight into the three-dimensional molecular structures. Figure 11 shows the molecular structures of methyl (or dimethyl) esters of the corresponding compounds, which have their energies minimized using universal force field (UFF) parameters.[56] Methyl esters, instead of 2-ethylhexyl esters, are shown in the figure in order to emphasize the structure of the molecular framework. The framework structure of these compounds is insensitive to the nature of the alkyl group in the ester chains. The phenyl ring/carboxyl frameworks in EHB and DEHP (as represented by methyl benzoate (a) and dimethyl phthalate (b)) are comparatively planar, although the repulsive steric interaction of oxygen atoms in the two ester groups in DEHP forces the carboxyl groups slightly out of the plane of the phenyl ring. Owing to the three-dimensional nature of the

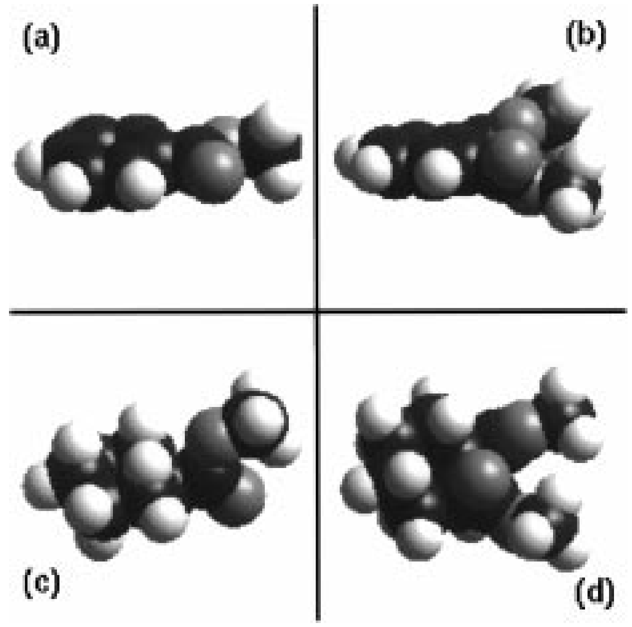

Figure 11. Molecular structure of (a) methyl benzoate, (b) dimethyl phthalate, (c) methyl cyclohexanecarboxylate, and (d) dimethyl *cis*-cyclohexane-1,2-dicarboxylate. The structures have their energies minimized using universal force field (UFF) parameters.[56] Methyl esters, instead of 2-ethylhexyl esters, are shown in this comparison of the molecular framework of the compounds studied.

cyclohexane ring, the framework of EHC appears to have a high degree of anisotropy, being close to a prolate shape (as represented in Figure 11c by a methyl ester). The anisotropy as well as the internal motions of the cyclohexane ring contributes to a lowering of the β values of the cyclohexane ring carbons in EHC. The smaller difference in β values between C/D (0.13) and E (0.15) in EHC compared to the corresponding carbons (0.32/0.34 for C/D and 0.47 for E) in EHB implies that the effect of the internal motion of the cyclohexane ring may be prevailing over the effect of anisotropy. By the addition of a second ester chain to the nonplanar cyclohexane ring, the anisotropy of DEHHP seems to be reduced, by an amount greater than that accompanying the addition of a second ester group to the planar phenyl ring (in DEHP). This agrees with the results shown in Figure 10, where the lowering of β values in flexible DEHHP ring carbons compared to DEHP is smaller than the lowering of β values in EHC compared to EHB. Thus despite the internal motions of the flexible cyclohexane ring which tend to reduce β values, the β values of the DEHHP ring carbons are relatively high due to the greatly reduced anisotropy.

Conclusion

The change in both the macroscopic physical properties and the microscopic motional behavior of the complex phthalate liquids arising from a structural variation in the molecular framework could be explained in terms of the characteristic of the structural components and their arrangements. The conjugation between a phenyl ring and carboxyl groups makes the structural framework stiffer and resulted in an enhanced viscosity. The Cole−Davidson distribution model was successfully applied to the ^{13}C NMR relaxation data to provide useful and detail information on the dynamic structure of the complex liquids. The motional behavior of these compounds was significantly affected by the shape of the molecular framework, which could be represented by the parameter β in the Cole−Davidson distribution model.

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