

High-pressure nuclear-magnetic-resonance study of carbon-13 relaxation in 2-ethylhexyl benzoate and 2-ethylhexyl cyclohexanecarboxylate

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Natural abundance carbon-13 spin-lattice relaxation times and ^{13}C - ^1H nuclear Overhauser enhancement (NOE) times of 2-ethyl hexylbenzoate (EHB) and 2-ethyl hexylcyclohexanecarboxylate (EHC) have been measured along isotherms of $-20, 0, 20, 40,$ and 80°C at pressures of 1–5000 bars using high-pressure, high-resolution NMR techniques. The ability to use pressure as an experimental variable has allowed us to study a wide range of molecular motions from extreme narrowing into the slow motional regime. In addition, the high-resolution capability even at high pressure permits the measurement of ^{13}C and NOE for each individual carbon in the molecules studied. Relaxation in both molecules is successfully analyzed in terms of a model assuming a Cole–Davidson distribution of correlation times. The comparison of parameters used in the model demonstrates the increased flexibility of the EHC ring over the EHB ring and also shows how the presence of the flexible ring contributes to the increased over-all mobility of the EHC molecule. The analysis of molecular reorientations in terms of activation volumes also indicates that EHB motion is highly restricted at low temperature.

INTRODUCTION

In previous papers^{1–3} we have discussed the results of variable pressure and temperature studies of the diffusion and relaxation behavior in the model lubricants 2-ethylhexyl benzoate (EHB) and 2-ethylhexyl cyclohexanecarboxylate (EHC). Both EHB and EHC are shown in Fig. 1 and are numbered according to international rules.

Our work dealing with the molecular dynamics of model lubricants was motivated by the need to understand these systems at the molecular level.⁴ While many dynamical NMR studies have been performed on simple liquids,⁵ long-chain *n*-alkanes,^{6–8} polymers, and biological polymers,^{5,9,10} such studies on complex hydrocarbons are limited. Studying molecular motion in EHB and EHC allows us to perform a systematic study of complex liquids which are representatives of actual lubricants. Indeed, research on such systems will help to understand how molecular structure affects important lubrication properties.

We have specifically measured natural abundance ^{13}C spin-lattice relaxation times, T_1 's, in EHB and EHC from pressures of 1–5000 bars along $-20, 0, 20, 40,$ and 80°C isotherms. We have also measured nuclear Overhauser enhancements (NOE's) under similar conditions. The dependences of the ^{13}C T_1 and NOE on the spectral density function^{9,11,12} $J(\omega)$ are as follows:

$$\frac{1}{T_{1\text{C}}} = \frac{1}{10} \frac{\gamma_{\text{H}}^2 \gamma_{\text{C}}^2 \hbar^2}{r_{\text{CH}}^6} \times [J_0(\omega_{\text{H}} - \omega_{\text{C}}) + 3J_1(\omega_{\text{C}}) + 6J_2(\omega_{\text{H}} + \omega_{\text{C}})], \quad (1)$$

$$\text{NOE} = 1 + \frac{\gamma_{\text{H}}}{\gamma_{\text{C}}} \times \frac{6J_2(\omega_{\text{H}} + \omega_{\text{C}}) - J_0(\omega_{\text{H}} + \omega_{\text{C}})}{J_0(\omega_{\text{H}} - \omega_{\text{C}}) + 3J_1(\omega_{\text{C}}) + 6J_2(\omega_{\text{H}} + \omega_{\text{C}})}. \quad (2)$$

In the above expressions, γ_{H} and γ_{C} are the proton and carbon gyromagnetic ratios, ω_{H} and ω_{C} are the proton and carbon Larmor frequencies, and r_{CH} is the carbon–hydrogen bond length. It is theoretically possible that carbon-13 spin-lattice relaxation measurements can be used to obtain information on the molecular dynamics of compounds in the liquid state,^{5–7,13} but it is necessary that a proper form of the spectral density function be found. In the simplest scenario, it can be assumed that a particular C–H relaxation vector reorients isotropically. The spectral density function is dependent on a single correlation time τ and has the form¹³

$$J(\omega) = \tau / (1 + \omega^2 \tau^2). \quad (3)$$

The correlation time is directly related to a rotational diffusion coefficient by¹⁴

$$\tau = 1/6D. \quad (4)$$

A more realistic premise is described by a model assuming anisotropic rotation. Three diffusion coefficients $D_x, D_y,$ and D_z describe rotation around three principal axes of an ellipsoid.^{10,15} In the axially symmetric case where $D_x = D_y,$

$$J(\omega) = \sum_{i=0}^z B_{i0}(\theta) \frac{[6D_x + i^2(D_z - D_x)]^{-1}}{1 + \omega^2 [6D_x + i^2(D_z - D_x)]^{-2}}, \quad (5)$$

where θ is the angle between the relaxation vector and the z axis, and the elements of the B matrix are given by London and Avitabile.¹⁶ The axially symmetric anisotropic rotation model is mathematically equivalent to a model assuming free internal rotation and isotropic overall motion.^{10,17}

$$J(\omega) = \sum_{i=0}^z \beta_{i0}(\theta) \frac{(6D_0 + i^2D_i)^{-1}}{1 + \omega^2 (6D_0 + i^2D_i)^{-2}}. \quad (6)$$

It can be seen that Eqs. (5) and (6) are equivalent if one assumes the internal diffusion coefficient

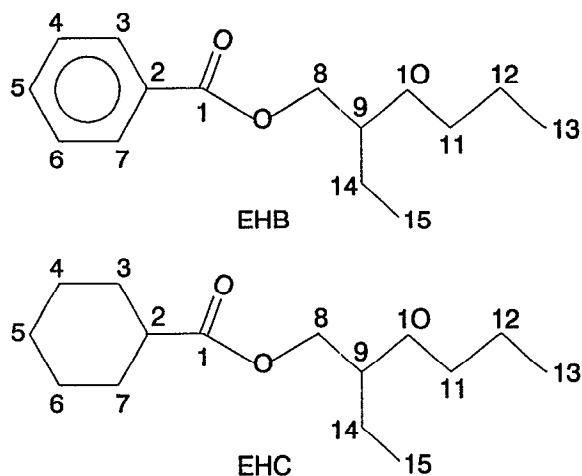


FIG. 1. Structural formulas of EHB and EHC. All carbons are numbered according to international rules.

$D_i = D_z - D_x = D_z - D_y$, and the overall diffusion coefficient $D_0 = D_x = D_y$.

However, in many instances it has been found that relaxation can only be described in terms of a distribution of correlation times.^{9,10,18-20} Writing the spectral density in terms of a distribution of isotropic reorientational correlation times gives⁹

$$J(\omega) = \int_0^{\infty} \frac{G(\tau)\tau d\tau}{1 + \omega^2\tau^2}, \quad (7)$$

where $G(\tau)$ is a probability density function such that

$$\int_0^{\infty} G(\tau) d\tau = 1. \quad (8)$$

The function $G(\tau)$ can take a number of forms, including a Gaussian,¹⁹ chi-squared,^{9,21,22} and the Cole–Davidson distribution.¹⁸⁻²⁰ Both the chi-squared and Cole–Davidson distributions have been used in cases where wide ranges of correlation times have been covered, but the chi-squared distribution seems to lend itself to systems where extremely long correlation times are present, as in polymer and biological macromolecular systems.^{9,21,22} The Cole–Davidson distribution, with a characteristic limiting correlation time τ_0 , has successfully described reorientation in glycerol, propylene glycol, and *n*-propanol.¹⁸⁻²⁰ The probability density function takes the form¹⁹

$$G(\tau) = \begin{cases} [\sin(\beta\pi)/\pi] (\tau/\tau_0 - \tau)^\beta & \text{for } 0 \leq \tau < \tau_0 \\ 0 & \text{for } \tau \geq \tau_0. \end{cases} \quad (9)$$

In Eq. (9), β is the distribution width and may assume a value from 0 to 1. When $\beta = 1$, this implies that one correlation time is present and the resulting spectral density function is equal to that of the isotropic model. As β approaches 0, the distribution becomes wider until infinitely many correlation times are assumed in the $\beta = 0$ limit. The average correlation time $\bar{\tau} = \beta\tau_0$ and the spectral density is²⁰

$$J(\omega) = \frac{\sin[\beta \arctan(\omega\tau_0)]}{\omega [1 + (\omega\tau_0)^2]^{\beta/2}}. \quad (10)$$

EXPERIMENT

The EHB sample was synthesized by Palmer Research Ltd. (United Kingdom). EHC was prepared in our laboratory by coupling 2-ethylhexanol with cyclohexane carbonyl chloride in the presence of dimethyl aniline. Further details of the synthesis were given previously.³

Proton decoupled carbon-13 spectra were obtained at 45.286 MHz using a homebuilt spectrometer interfaced to a General Electric 293D programmable pulser and a Nicolet 1280 computer. Details of the spectrometer, probe, and experimental procedure were discussed previously.³ The measurements of T_1 values are estimated to have an accuracy of $\pm 10\%$. The accuracy of NOE measurements is estimated to be within $\pm 10\%$ for higher values and within $\pm 15\%$ for lower values. Pressures are accurate to ± 10 bar and temperatures are accurate to ± 0.5 °C.

RESULTS AND DISCUSSION

Since this work is the first experimental NMR study which investigates both the temperature and pressure dependence of the relaxation behavior of each individual carbon in the complex liquids, we hope that the data will stimulate theoretical effort aimed at improving our understanding of motional dynamics in complex liquids. For this reason, we include Tables I and II, which give the experimental $^{13}\text{CNT}_1$'s (where N is the number of directly attached protons) of EHB and EHC. Values are shown for all EHB carbons except 1 and 2, which are not directly attached to any protons. The EHC NT_1 values are reported for all carbons except carbon 1. Because separate NMR peaks were not resolvable for EHC carbons 3 and 11, a single NT_1 value is shown for both carbons at each pressure and temperature. Omissions in each table indicate that measurement of the T_1 was precluded either by a low signal-to-noise ratio or an inability to resolve the resonance peak at that temperature and pressure.

Attempts were made to analyze the NT_1 data in terms of the models discussed in the Introduction. The simplest approach, the isotropic model, assumed that one correlation time described reorientation for each of the carbons in EHB and EHC. It was assumed that reorientation followed an Arrhenius-type pressure dependence:

$$\tau = \tau_i \exp(\Delta V^\ddagger P/RT), \quad (11)$$

where τ_i is a preexponential factor and ΔV^\ddagger is an activation volume. The analysis involved substituting Eq. (11) into Eq. (3) and using the resulting form of the spectral density function in Eq. (1). Equation (1), now written in terms of two adjustable parameters, τ_i and ΔV^\ddagger , was used to fit experimental NT_1 vs pressure plots. The experimental data was fitted with a computer program which searched parameter space for a minimum value of χ^2 given by

$$\chi^2 = \sum_{i=1}^n \left[\frac{T_1(\text{expt}) - T_1(\text{calc})}{T_1(\text{expt})} \right]^2, \quad (12)$$

where n is the number of experimental T_1 values for a given carbon. Not surprisingly, the isotropic model failed to adequately describe relaxation behavior in either EHB or EHC.

A similar approach to the isotropic analysis was taken to

TABLE I. ^{13}C spin-lattice relaxation times (NT_1 's) of EHB. All times are expressed in seconds.

	3	4	5	8	9	10	11	12	13	14	15
$T = -20^\circ\text{C}$											
1	0.127	0.128	0.0951	0.138	0.121	0.195	0.274	0.396	1.71	0.212	1.30
250	0.109	0.110	0.0916	0.122	0.108	0.170	0.228	0.312	1.47	0.178	1.18
500	0.113	0.114	0.116	0.131	0.116	0.163	0.214	0.274	1.31	0.176	1.10
750	0.134	0.136	0.154	0.151	0.138	0.171	0.210	0.260	1.23	0.188	1.07
1000	0.178	0.183	0.228	0.204	0.178	0.200	0.230	0.262	1.23	0.214	1.09
1250	0.241	...	0.330	0.262	0.223	0.220	0.244	0.272	1.23	...	1.13
1500	0.278	0.255	0.226	0.252	0.272	1.24	...	1.15
1750	0.327	...	0.284	0.302	1.26	...	1.18
$T = 0^\circ\text{C}$											
1	0.261	0.256	0.164	0.258	0.230	0.398	0.582	0.922	3.33	0.406	2.61
250	0.201	0.197	0.123	0.196	0.174	0.302	0.442	0.708	2.75	0.320	2.14
500	0.161	0.160	0.111	0.176	0.152	0.262	0.372	0.570	2.63	0.270	1.91
750	0.128	0.126	0.0960	0.136	0.120	0.202	0.306	0.456	2.21	0.216	1.64
1000	0.109	0.107	0.0840	0.124	0.110	0.181	0.244	0.374	1.88	0.189	1.42
1250	0.106	0.108	0.0920	0.113	0.110	0.174	0.242	0.348	1.76	0.177	1.34
1500	0.106	0.109	0.106	0.125	0.110	0.171	0.238	0.322	1.68	0.182	1.33
1750	0.120	0.127	0.141	0.147	0.121	0.180	0.220	0.294	1.65	0.175	1.31
2000	0.134	0.138	0.192	0.148	0.134	0.178	0.234	0.290	1.62	0.188	1.30
2250	0.167	0.183	0.213	0.176	0.169	0.206	0.232	0.294	1.50	0.189	1.29
2500	0.195	0.202	0.302	0.166	0.179	0.208	0.240	0.290	1.53	0.208	1.33
2750	0.264	0.279	0.392	0.191	0.232	0.238	0.248	0.276	1.57	0.230	1.38
3000	0.298	0.285	0.234	0.260	0.308	1.57	...	1.36
$T = 20^\circ\text{C}$											
1	0.583	0.578	0.344	0.573	0.501	0.876	1.28	1.96	6.03	0.888	4.62
250	0.456	0.458	0.269	0.456	0.396	0.718	1.04	1.66	5.73	0.734	4.06
500	0.340	0.342	0.206	0.344	0.293	0.530	0.818	1.32	4.98	0.560	3.59
750	0.267	0.268	0.162	0.269	0.240	0.442	0.672	1.06	4.44	0.452	3.18
1000	0.214	0.215	0.135	0.214	0.193	0.354	0.532	0.834	3.93	0.352	2.69
1250	0.181	0.183	0.119	0.186	0.170	0.302	0.460	0.744	3.39	0.324	2.51
1500	0.150	0.153	0.106	0.159	0.147	0.258	0.392	0.620	3.18	0.284	2.19
1750	0.130	0.130	0.0991	0.143	0.128	0.224	0.342	0.522	2.83	0.244	2.02
2000	0.119	0.121	0.0921	0.132	0.118	0.208	0.304	0.460	2.52	0.224	1.84
2250	0.108	0.110	0.0872	0.130	0.110	0.190	0.284	0.420	2.31	0.206	1.61
2500	0.107	0.106	0.103	0.129	0.111	0.179	0.262	0.378	2.21	0.193	1.59
2750	0.104	0.107	0.102	0.126	0.109	0.171	0.250	0.344	2.05	0.183	1.49
3000	0.112	0.115	0.125	0.136	0.116	0.185	0.240	0.327	1.91	0.187	1.50
3250	0.126	0.131	0.153	0.148	0.129	0.189	0.242	0.314	1.85	0.192	1.46
3500	0.140	0.145	0.175	0.168	0.141	0.196	0.242	0.294	1.82	0.198	1.47
3750	0.162	...	0.219	0.184	0.158	0.212	0.244	0.290	1.77	0.214	1.47
4000	0.192	...	0.264	0.208	0.180	0.218	0.254	0.290	1.80	0.226	1.47
4250	0.231	...	0.343	0.248	0.204	0.232	0.262	0.296	1.81	0.236	1.52
4500	0.272	0.224	0.248	0.270	0.298	1.80	...	1.54
4750	0.300	0.241	0.250	0.272	0.302	1.85	...	1.52
5000	0.320	0.259	...	0.278	0.316	1.80	...	1.56
$T = 40^\circ\text{C}$											
1	1.29	1.29	0.733	1.25	1.05	1.85	2.80	4.04	10.8	1.81	8.14
250	0.971	0.970	0.550	0.923	0.814	1.43	2.18	3.40	9.24	1.50	7.26
500	0.729	0.726	0.418	0.724	0.631	1.13	1.72	2.66	8.58	1.16	6.29
1000	0.444	0.447	0.260	0.442	0.397	0.728	1.12	1.82	6.87	0.766	4.89
1500	0.294	0.294	0.175	0.302	0.268	0.496	0.780	1.27	5.70	0.534	3.98
2000	0.211	0.214	0.137	0.219	0.195	0.370	0.572	0.936	4.68	0.394	3.24
2500	0.152	0.152	0.104	0.169	0.143	0.274	0.408	0.680	3.69	0.298	2.43
2750	0.135	0.137	0.102	0.154	0.137	0.246	0.382	0.596	3.42	0.262	2.22
3000	0.122	0.126	0.0930	0.144	0.120	0.224	0.350	0.538	3.03	0.248	1.98
3500	0.110	0.113	0.0942	0.129	0.115	0.206	0.304	0.444	2.72	0.226	1.94
4000	0.106	0.109	0.104	0.129	0.110	0.193	0.272	0.380	2.38	0.202	1.76
4500	0.111	0.117	0.124	0.145	0.115	0.189	0.254	0.346	2.15	0.202	1.66
5000	0.132	0.141	0.175	0.160	0.138	0.204	0.264	0.314	...	0.210	1.63
$T = 80^\circ\text{C}$											
1	3.36	3.32	1.86	3.21	2.76	4.54	6.92	9.78	20.6	4.67	16.3
500	2.09	2.06	1.15	1.99	1.73	3.02	4.62	6.94	17.8	3.06	13.4
1000	1.40	1.41	0.784	1.33	1.18	2.12	3.34	5.14	14.4	2.19	11.1
1500	0.992	0.986	0.553	0.950	0.867	1.56	2.48	3.96	13.8	1.66	9.51
2000	0.717	0.710	0.387	0.676	0.622	1.16	1.82	3.00	11.7	1.26	8.07
2500	0.498	0.507	0.280	0.482	0.462	0.876	1.40	2.36	10.1	0.962	6.83
3000	0.389	0.390	0.225	0.394	0.361	0.708	1.12	1.84	8.76	0.795	5.79
3500	0.310	0.312	0.188	0.316	0.290	0.594	0.916	1.47	7.86	0.650	5.19
4000	0.242	0.248	0.144	0.252	0.237	0.456	0.740	1.17	6.69	0.528	4.41
4500	0.193	0.200	0.130	0.216	0.193	0.396	0.608	0.980	5.88	0.442	2.60
5000	0.165	0.171	0.117	0.177	0.166	0.332	0.506	0.790	4.89	0.370	2.24

TABLE II. ¹³C spin-lattice relaxation times (*NT*1's) of EHC. All times are expressed in seconds.

	2	3,11	4	5	8	9	10	12	13	14	15
<i>T</i> = -20 °C											
1	0.328	0.408	0.422	0.256	0.186	0.153	0.260	0.530	2.03	0.270	1.64
250	0.254	0.302	0.312	0.199	0.138	0.119	0.192	0.394	1.65	0.208	1.34
500	0.232	0.278	0.284	0.204	0.134	0.115	0.188	0.374	1.61	0.189	1.28
750	0.213	0.232	0.236	0.188	0.130	0.112	0.165	0.296	1.35	0.178	1.11
1000	0.209	0.226	0.228	0.196	0.130	0.114	0.173	0.288	1.36	0.182	1.13
1250	0.212	0.214	0.212	...	0.142	0.133	0.175	0.262	1.25	0.184	1.07
1500	0.206	0.214	0.210	...	0.155	0.139	0.181	0.262	1.26	0.194	1.09
1750	0.212	0.214	0.210	...	0.172	0.164	0.191	0.256	1.22	0.200	1.10
2000	0.222	0.222	0.218	...	0.204	0.180	0.206	0.260	1.21	...	1.09
2250	0.235	0.226	0.230	...	0.228	0.201	0.218	0.256	1.20	...	1.12
2500	0.238	0.244	0.246	...	0.274	0.219	...	0.254	1.20	...	1.12
2750	0.255	0.248	0.250	...	0.264	0.241	...	0.258	1.11	...	1.04
3000	0.249	0.268	0.298	0.280	1.12	...	1.09
3250	1.13	...	1.10
3500	1.15	...	1.09
<i>T</i> = 0 °C											
1	0.640	0.884	0.386	0.498	0.380	0.313	0.557	1.20	3.96	0.581	3.10
250	0.494	0.674	0.670	0.370	0.282	0.235	0.424	0.930	3.54	0.438	2.70
500	0.376	0.502	0.508	0.298	0.216	0.178	0.322	0.728	2.94	0.336	2.20
750	0.330	0.434	0.436	0.250	0.184	0.157	0.280	0.638	2.79	0.294	2.04
1000	0.275	0.360	0.358	0.232	0.158	0.133	0.244	0.522	2.40	0.254	1.78
1250	0.252	0.310	0.308	0.206	0.138	0.120	0.206	0.460	2.22	0.222	1.64
1500	0.234	0.276	0.274	0.196	0.143	0.113	0.198	0.408	2.04	0.206	1.55
1750	0.220	0.252	0.248	0.186	0.125	0.110	0.183	0.360	1.90	0.194	1.44
2000	0.208	0.236	0.226	0.190	0.137	0.107	0.184	0.334	1.75	0.188	1.37
2250	0.203	0.222	0.214	0.190	0.133	0.114	0.170	0.316	1.70	0.183	1.32
2500	0.201	0.218	0.214	0.206	0.156	0.124	0.188	0.308	1.63	0.186	1.31
2750	0.208	0.214	0.202	...	0.146	0.135	0.184	0.290	1.58	0.188	1.28
3000	0.207	0.218	0.208	...	0.167	0.153	0.196	0.284	1.54	0.204	1.30
3250	0.215	0.216	0.206	...	0.162	0.159	0.197	0.276	1.52	0.202	1.30
3500	0.219	0.216	0.214	...	0.186	0.173	0.210	0.273	1.48	0.213	1.28
3750	0.223	0.224	0.210	...	0.204	0.186	0.212	0.266	1.49	0.210	1.28
4000	...	0.228	0.226	0.198	0.222	0.276	1.49	...	1.28
4250	...	0.240	0.230	0.254	0.246	0.264	1.46	...	1.28
4500	...	0.244	0.252	...	0.264	1.41	...	1.28
<i>T</i> = 20 °C											
1	1.32	1.82	1.86	0.938	0.782	0.650	1.11	2.50	6.85	1.17	5.32
250	1.03	1.43	1.44	0.705	0.606	0.479	0.901	2.05	6.03	0.942	4.77
500	0.812	1.16	1.16	0.626	0.502	0.412	0.758	1.74	5.80	0.786	4.35
750	0.673	0.934	0.940	0.492	0.384	0.324	0.602	1.45	5.29	0.632	3.81
1000	0.507	0.732	0.728	0.388	0.302	0.252	0.474	1.17	4.68	0.498	3.36
1250	0.428	0.600	0.596	0.330	0.248	0.212	0.394	0.964	4.17	0.418	2.97
1500	0.367	0.508	0.506	0.288	0.208	0.183	0.342	0.816	3.81	0.356	2.64
1750	0.325	0.446	0.436	0.250	0.186	0.160	0.292	0.708	3.45	0.316	2.41
2000	0.287	0.390	0.384	0.236	0.164	0.144	0.266	0.648	3.18	0.286	2.22
2250	0.266	0.338	0.330	0.214	0.152	0.129	0.240	0.566	2.88	0.256	2.02
2500	0.245	0.308	0.298	0.193	0.139	0.122	0.214	0.484	2.69	0.234	1.91
2750	0.229	0.282	0.276	0.202	0.130	0.144	0.208	0.462	2.54	0.218	1.82
3000	0.225	0.258	0.252	0.191	0.131	0.115	0.198	0.422	2.37	0.214	1.71
3250	0.210	0.242	0.234	0.194	0.137	0.109	0.190	0.388	2.24	0.204	1.65
3500	0.206	0.234	0.224	0.185	0.135	0.109	0.189	0.372	2.12	0.199	1.59
3750	0.198	0.222	0.212	0.185	0.138	0.115	0.187	0.350	2.04	0.195	1.56
4000	0.195	0.214	0.200	0.192	0.145	0.120	0.188	0.330	1.97	0.192	1.52
4250	0.195	0.206	0.194	0.174	0.143	0.126	0.184	0.322	1.93	0.184	1.51
4500	0.194	0.210	0.197	...	0.170	0.137	0.195	0.304	1.81	0.202	1.46
4750	0.193	0.212	0.200	...	0.167	0.150	0.206	0.288	1.75	0.210	1.41
5000	0.200	0.220	0.204	...	0.178	0.161	0.214	0.292	1.75	0.218	1.40
<i>T</i> = 40 °C											
1	2.33	3.18	3.30	1.53	1.41	1.16	2.01	4.44	10.8	1.98	8.32
500	1.38	1.99	1.98	0.985	0.852	0.707	1.30	2.93	8.54	1.31	6.48
1000	0.918	1.33	1.32	0.654	0.560	0.458	0.890	2.12	7.17	0.946	5.13
1500	0.607	0.887	0.875	0.450	0.367	0.309	0.590	1.47	5.82	0.565	4.05
2000	0.462	0.644	0.629	0.347	0.275	0.228	0.440	1.09	4.76	0.484	3.27
2500	0.347	0.485	0.477	0.290	0.218	0.178	0.353	0.811	4.03	0.373	2.80
3000	0.284	0.388	0.377	0.237	0.174	0.151	0.285	0.677	3.44	0.310	2.39
3500	0.254	0.331	0.317	0.227	0.159	0.135	0.256	0.598	3.21	0.280	2.20
4000	0.222	0.282	0.270	0.202	0.152	0.123	0.222	0.488	2.66	0.260	1.97
4500	0.208	0.252	0.238	0.196	0.145	0.118	0.206	0.436	2.60	0.218	1.85
5000	0.200	0.230	0.218	0.192	0.145	0.112	0.200	0.388	2.29	0.214	1.70

TABLE II (continued).

	2	3,11	4	5	8	9	10	12	13	14	15
$T = 80\text{ }^\circ\text{C}$											
1	5.20	7.44	7.62	4.40	3.58	2.84	5.00	10.3	21.1	5.12	17.3
500	3.17	4.66	4.62	2.48	2.04	1.74	3.12	7.06	17.1	3.22	14.1
1000	2.35	3.58	3.50	1.83	1.54	1.30	2.40	5.49	15.8	2.54	11.6
1500	1.67	2.52	2.48	1.33	1.11	0.927	1.73	4.10	13.0	1.88	9.67
2000	1.18	1.85	1.81	0.954	0.754	0.671	1.32	3.30	11.5	1.41	8.17
2500	0.931	1.48	1.44	0.744	0.642	0.561	1.06	2.67	10.5	1.18	6.98
3000	0.701	1.12	1.07	0.596	0.470	0.419	0.838	2.10	8.83	0.930	6.05
3500	0.576	0.842	0.874	0.500	0.378	0.339	0.692	1.75	7.95	0.772	5.29
4000	0.497	0.614	0.712	0.408	0.324	0.281	0.578	1.43	7.20	0.646	4.69
4500	0.402	0.602	0.570	0.356	0.266	0.234	0.476	1.16	6.19	0.536	4.19
5000	0.356	0.518	0.490	0.310	0.222	0.208	0.410	1.00	5.57	0.468	3.80

try and describe the motions of EHB and EHC in terms of the axially symmetric-free-internal-rotation model. An Arrhenius-type dependence as in Eq. (11) was assumed for each rotational diffusion coefficient. As expected, even this analysis did not reproduce the experimental relaxation data.

An attempt was then made to analyze the experimental NT_1 data in terms of a model assuming a Cole–Davidson distribution of correlation times. It was assumed that the limiting correlation time τ_0 had an Arrhenius-type dependence as in Eq. (11). The Cole–Davidson form of $J(\omega)$ therefore possessed three adjustable parameters: τ_{0i} (the preexponential factor for the limiting correlation time), β (the distribution width), and ΔV^\ddagger . It is evident that τ_{0i} and ΔV^\ddagger are pressure-independent parameters, but it is unclear as to whether β should be pressure independent. It has been shown in our study of glycerol that the value of β cannot uniquely be determined in the extreme narrowing region,²⁰ so the question as to whether β is dependent on pressure is moot under conditions of fast molecular motion. But under conditions where $\omega\tau > 1$, β becomes important in determining the value of $J(\omega)$. As β changes, it will subsequently change the NT_1 minimum value occurring in a plot of NT_1 vs correlation time.^{19,20} In our study²⁰ mentioned earlier, β values for deuterium relaxation in glycerol- d_4 and glycerol- d_3 were determined to be only weakly pressure dependent since in each fluid the minima of different isobaric T_1 vs (temperature)⁻¹ plots had similar T_1 values. Figures 2(a)–2(d) show representative plots of the temperature dependences of EHB and EHC ^{13}C NT_1 's. It is apparent that for each carbon shown in the figure the magnitude of NT_1 at its minimum does not change appreciably with pressure. Within experimental error, the NT_1 minima were found to be pressure independent for all other carbons studied, and therefore it was assumed that β was pressure independent in EHB and EHC liquids.

The representative fits of EHB and EHC NT_1 's plotted against pressure using the Cole–Davidson distribution model are shown in Figs. 3(a)–3(c). The model clearly represents the experimental points well. The three figures, at temperatures of -20 , 20 , and $40\text{ }^\circ\text{C}$ give a general picture of how the relaxation behavior in the two fluids change with temperature and pressure. At $-20\text{ }^\circ\text{C}$, shown in Fig. 3(a), the motions of the EHB ring-5 carbons, the methine-9 chain

carbon, are in the slow-motion regime. The corresponding nuclei in EHC also possess NT_1 values which are in the slow-motion regime, but the NT_1 vs P curves show much more shallow minima. The wider minima found for the EHC data reflect the greater mobilities of the EHC carbons over those in EHB. At $20\text{ }^\circ\text{C}$, shown in Fig. 3(b), there are considerable differences in relaxation behavior of the EHB and EHC rings, and the carbon-5 in EHC clearly exhibits a greater mobility. The behavior of the methine carbons in the two molecules are much more similar at $20\text{ }^\circ\text{C}$ than at $-20\text{ }^\circ\text{C}$. Even at $40\text{ }^\circ\text{C}$, the EHC ring still seems to show a greater mobility than the EHB ring, in contrast to the EHB and EHC methine carbons which show nearly identical motional characteristics. The EHC methine carbon only shows a greater mobility over the EHB methine carbon at lower temperatures. The differences which exist in the relaxation behaviors of the EHB and EHC methine carbons parallel trends occurring in the fluids' viscosities, as it was found that EHC has a significantly lower viscosity than EHB at low temperatures and high pressures.³ Considering that the rates of overall molecular motions can be related to viscosities through the Debye expression, one expects that at low temperatures the rate of overall molecular motion in EHB is slower than in EHC.

The Cole–Davidson distribution model has been found to represent ^{13}C NT_1 data well for EHB and EHC carbons 3, 4, 5 (ring carbons), 8, 9, 10, 11, and 14. For carbons 12, 13, and 15, attempts to fit the data resulted in extremely low values of β (< 0.02). Such values have no physical meaning, and we attribute the failure to the fact that most of the data for these methyl carbon nuclei lay in the extreme narrowing region where a unique value of β is difficult to determine.

For cases where the Cole–Davidson distribution model has been able to fit the data, we must consider the validity of the model. With three adjustable parameters, it may be possible to fit the experimental data without truly representing the physical conditions of the systems. As a check we have attempted to reproduce the experimental NOE values from Eq. (2) using the optimized parameters of the NT_1 fits. Figures 4(a)–4(d) show representative plots of how calculated and experimental NOE values compare for carbons 5 and 9. The experimental data are typically reproduced well within $\pm 10\%$ and all of the data are reproduced well within

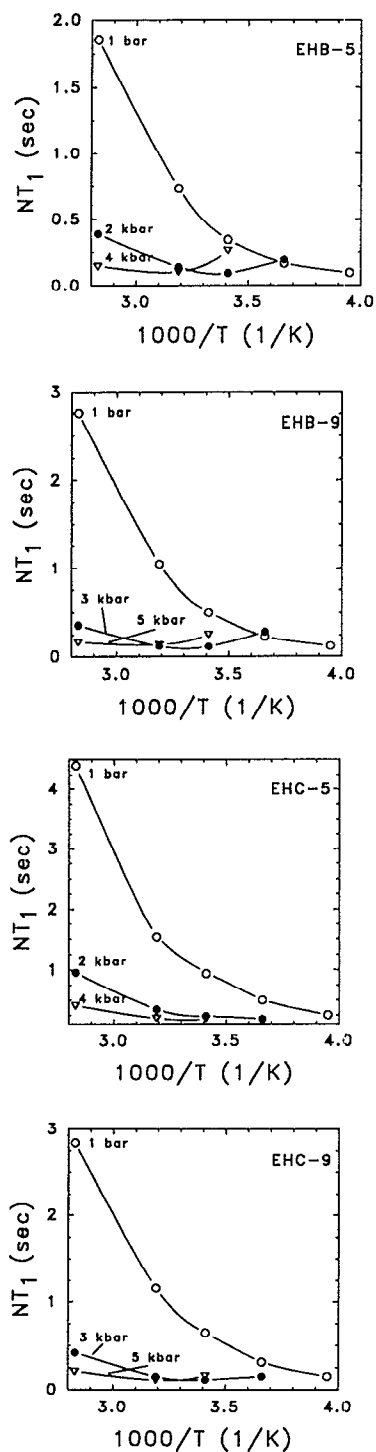


FIG. 2. Temperature dependence of ^{13}C NT_1 's in EHB and EHC. (a) EHB-5: 0, 1 bar; ●, 2 kbar; ▽, 4 kbar. (b) EHB-9: ○, 1 bar; ●, 3 kbar; ▽, 5 kbar. (c) EHC-5: ○, 1 bar; ●, 2 kbar; ▽, 4 kbar. (d) EHC-9: ○, 1 bar; ●, 3 kbar; ▽, 5 kbar.

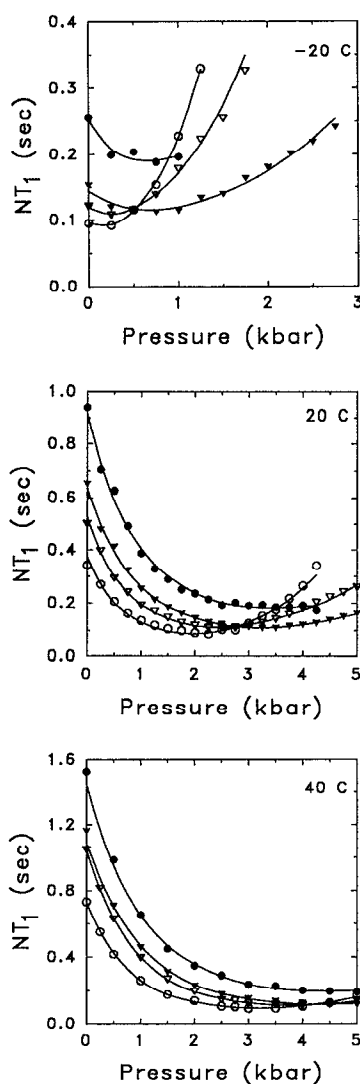


FIG. 3. Pressure dependence of EHB and EHC ^{13}C NT_1 's fitted by using the Cole-Davidson distribution model. (a) -20°C , (b) 20°C , (c) 40°C . In all plots, ○, EHB-5; ▽, EHB-9; ●, EHC-5; ▼, EHC-9.

$\pm 15\%$. A slight discrepancy seems to occur where the NOE falls below 1.6, as in the lower-temperature plots of EHB carbons 5 and 9 and EHC carbon 9. Though the experimental data trends are well represented in this region, predicted NOE values are consistently higher than experimental values. Low signal-to-noise conditions at the lower temperatures may have contributed to the discrepancy. Also, β may change with pressure. Again, we do not assume that β is pressure independent, but that it does not change enough to affect the fits within the experimental error.

Therefore, because NOE values predicted from the Cole-Davidson fits reproduce the experimental values within the assigned error limits, we feel confident about the ability of the model to describe ^{13}C relaxation in EHB and EHC.

The parameter β , being the distribution width, is an indication of the range of motions involved in the reorientation of a particular relaxation vector. As β approaches zero, a greater molecular flexibility is implied since a larger number of motions contribute to relaxation. Conversely, as β nears a value of one, fewer motions contribute to relaxation and a stiffness in the molecule is implied. Optimized values of β for carbons to which the Cole-Davidson distribution model is applicable are shown in Table III. It is apparent that the β value for each carbon remains relatively temperature independent over the range of -20 to 40°C . Average values of β in EHB and EHC are compared in Fig. 5. Most striking are the significantly lower ring β values in EHB. The decreased β values in EHC no doubt occur because the C-H vectors in the ring are not in any single plane, and rotation around any axis would relax all the spins. It is possible that increased flexibility in the EHC ring over the aromatic ring in EHB also contributes to the decreased EHC ring β values. It is

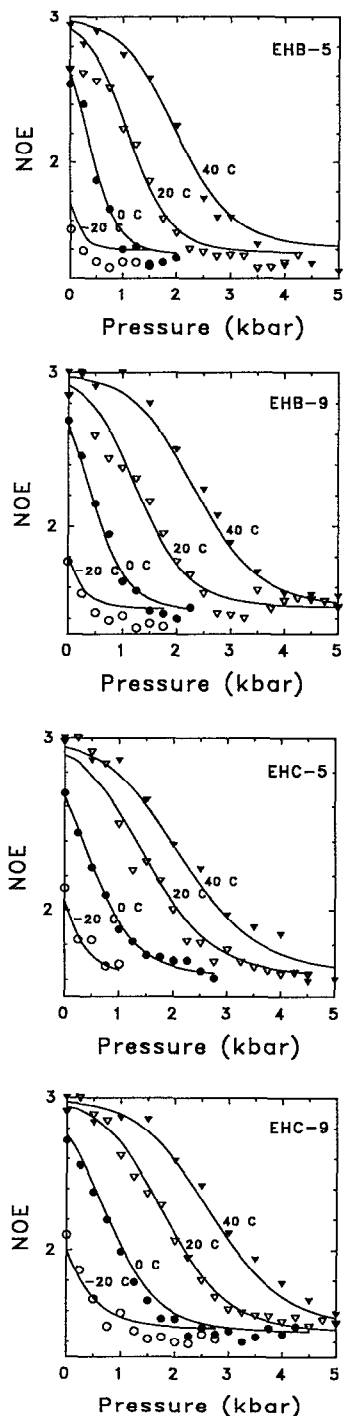


FIG. 4. Comparison of experimental nuclear Overhauser effect enhancements and NOE's calculated from the parameters optimized from the Cole-Davidson distribution model. (a) EHB-5, (b) EHB-9, (c) EHC-5, (d) EHC-9. In all plots, \circ , -20°C ; \bullet , 0°C ; ∇ , 20°C ; \blacktriangledown , 40°C .

also interesting to note that the para (5) carbon in EHB shows a significantly higher β value than the ortho (3) or meta (4) carbons. The lower β values of carbons 3 and 4 imply that a wider distribution of correlation times are associated with relaxation in these carbons than in carbon-5. A possible explanation may be that the ring rotates around an axis that runs through carbon-5 and hence through the carbon-5 relaxation vector (C-H bond). Relaxation could not be induced in carbon-5 by such a rotation since the relaxation vector does not change direction with such a motion. The β values are consistent with the observation in our pre-

TABLE III. Values of β determined from isothermal fits of NT_1 vs pressure for EHB and EHC.

C	-20°C	0°C	20°C	40°C	Average
EHB					
3,7	0.34	0.35	0.32	0.33	0.34
4,6	0.33	0.34	0.31	0.31	0.32
5	0.46	0.51	0.49	0.43	0.47
8	0.29	0.30	0.28	0.26	0.28
9	0.35	0.38	0.35	0.34	0.35
10	0.18	0.17	0.15	0.15	0.16
11	0.13	0.12	0.11	0.097	0.11
14	0.17	0.16	0.14	0.13	0.15
EHC					
2	0.13	0.14	0.14	0.13	0.14
3,7,11	0.13	0.13	0.13	0.11	0.13
4,6	0.13	0.13	0.14	0.12	0.13
5	0.15	0.15	0.16	0.14	0.15
8	0.26	0.26	0.26	0.22	0.26
9	0.32	0.35	0.35	0.32	0.34
10	0.18	0.16	0.15	0.13	0.16
14	0.16	0.16	0.14	0.12	0.15

vious paper³ that indicated reorientation along some symmetry axis. These points imply that the aromatic ring may rotate around the bond between carbons 1 and 2. Whether this type of rotation occurs in EHC is inconclusive, but rotation around the $\text{C}_1\text{-C}_2$ bond is certainly not unthinkable as it is a single bond and not a partial double bond as in EHB.³ In any case, reorientation behavior between the EHC ring carbons seems more uniform than in EHB.

It is also apparent that the β values of the chain carbons in EHB are very similar to corresponding values in EHC. In both cases the methine (9) carbon has the largest β value, no doubt because the C-H vector is relatively immobile with respect to internal rotation. Both molecules also show β at carbons 10, 11, and 14 which are significantly lower than corresponding methine β values. It was discussed previous-

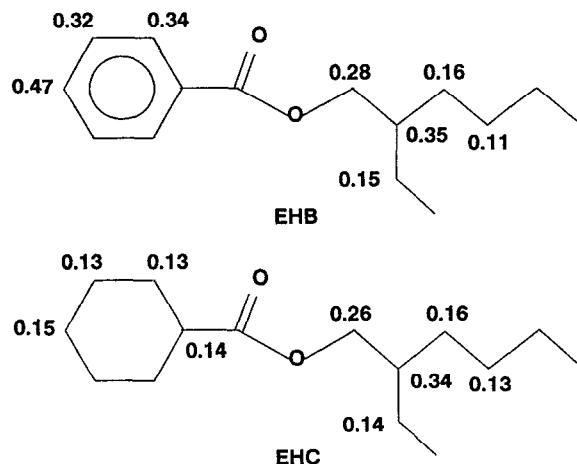


FIG. 5. Average values of the Cole-Davidson β distribution width for each of the analyzed carbons in EHB and EHC. See text for further details.

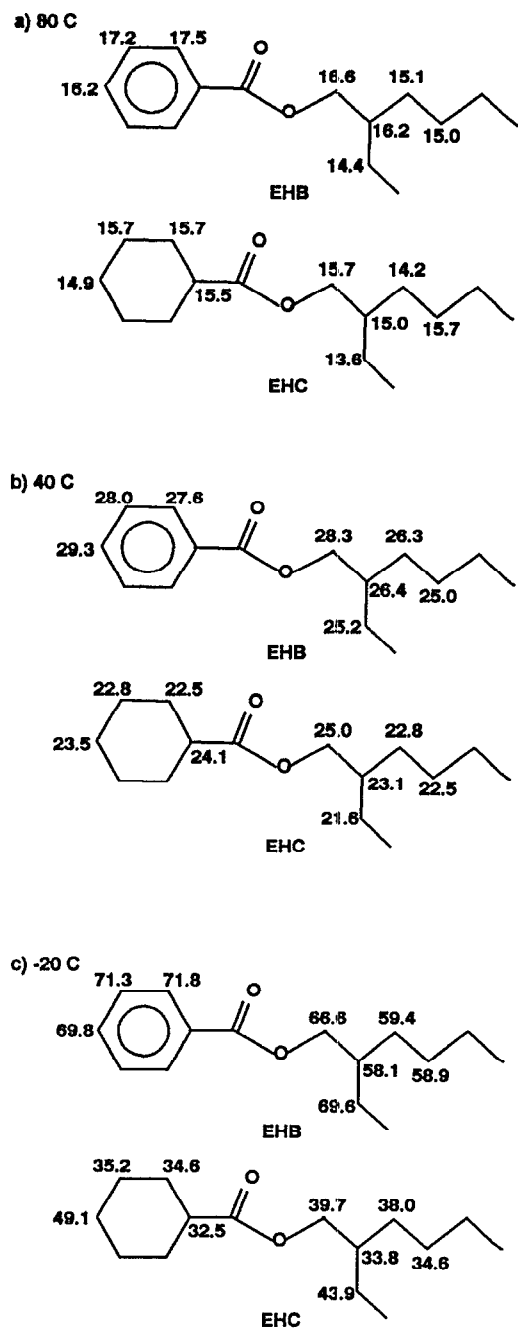


FIG. 6. Reorientational activation volumes calculated for individual carbons in EHB and EHC. Values in (a) at 80 °C were calculated from the log dependency of τ_{eff} on pressure. Values in (b) at 40 °C and in (c) at -20 °C were calculated from the fits of the NT_1 vs pressure data using the Cole-Davidson distribution model. See text for further details.

ly³ that mobility gradients probably exist along the chains in EHB and EHC, and there appears to be a decrease in β values for carbons further removed from the methine carbon. Because of the limited number of cases among the chain carbons to which the Cole-Davidson distribution model is applicable, though, it is difficult to state as to whether the values of β are indicative of mobility gradients.

The calculations used in the fitting of the EHB and EHC ¹³C NT_1 data have assumed that reorientation in these vis-

cus fluids is an activated process. Whether an activation-state analysis can be applied to molecular motion in liquids is certainly open to question.²³ The theory assumes the existence of a well-defined transition state, and this is certainly difficult to imagine in the case of a collection of reorienting molecules. The concept of an activated state may be an oversimplification of what is actually occurring during the diffusional process.²⁴ Nevertheless, analysis in terms of activation volumes has been shown to be a convenient qualitative way of comparing the relative pressure effects on reorientations.^{23,25}

Activation volumes calculated from the Cole-Davidson fits of NT_1 vs pressure plots (-20 and 40 °C) or calculated from the slope of the $\ln \tau_{\text{eff}}$ vs pressure plots (80 °C) are shown in Figs. 6(a)–6(c). Since the 80 °C NT_1 data lay in the extreme narrowing region, correlation times were calculated from the expression^{3,6,7}

$$\tau_{\text{eff}} = r_{\text{CH}}^6 / CNT_1, \quad (13)$$

where r_{CH} is the C-H internuclear distance and C is a constant equal to $3.56 \times 10^{10} \text{ \AA}^6 \text{ s}^{-1}$. At 80 °C, the reorientational activation volumes of EHB and EHC are very similar. Though slightly larger ΔV^\ddagger values are found in EHB at 80 °C, it is uncertain whether any significance can be associated with this observation due to the qualitative and simplistic nature of the analysis. At 40 °C, the activation volumes are larger compared to those at 80 °C for both molecules. Values of ΔV^\ddagger in EHB are significantly larger than corresponding values in EHC, and the most dramatic difference between the two molecules is observed at -20 °C. Figure 6(c) shows how activation volumes in EHB are 40%–100% larger than those in EHC. Large increases in the magnitudes of EHB aromatic ΔV^\ddagger values as well as in those of the EHB chain carbons from -20 to 40 °C demonstrate how certain motions become very restricted at lower temperatures. Because ΔV^\ddagger increases dramatically for all EHB carbons analyzed, this leads to the conclusion that some motion common to all nuclei in the molecules is severely restricted at -20 °C. Most likely, the common motion is the overall molecular motion, or it may be a more complex cluster motion.

The trend in the ΔV^\ddagger differences between EHB and EHC with temperature suggests that reorientation in the two liquids occurs with near equal facility at higher temperatures, but at lower temperatures EHB reorients with a much greater change in the fluid's local structure. This observation is interesting when one considers that EHC has a much lower compressibility than EHB.³ The presence of the flexible cyclohexyl ring probably allows the EHC molecule to change shape more easily than EHB to accommodate reorientation at higher densities.

In conclusion, the results of this study illustrate the promising future of high-pressure, high-resolution NMR techniques to yield unique data of high information content on motional dynamics of complex liquids. A wide spectrum of both basic and technological fields ranging from dynamics of biopolymers to lubrication will benefit from the improved understanding of dynamical behavior of complex liquids.

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