The Dynamics of Aromatic Ring Flipping in Solid 4,4′-Diphenoxydiphenylether as Studied by Carbon-13 tr-ODESSA NMR

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Abstract. The 1-D magic-angle spinning (MAS) nuclear magnetic resonance polarization transfer method, time-reverse one-dimensional exchange spectroscopy by side-band alternation (tr-ODESSA), was applied to the carbon-13 signals (at natural abundance) of a powder sample of 4,4′-diphenoxy-diphenyl ether. The T_1's of the various carbons in the sample are of the order of several thousands of seconds, allowing dynamic measurements to be carried out over long time periods. The carbon-13 MAS spectrum of 4,4′-diphenoxydiphenyl ether is only partially resolved, but there are enough well-defined peaks to allow a complete analysis of the dynamic processes in this compound. In the tr-ODESSA experiments, all of the carbon peaks showed a dispersion (sigmoidal reduction in the peak intensity) at a characteristic time of about 20 s, which is identified with a spin diffusion process. This sets an upper limit to the time range over which chemical (physical) processes can be measured by the tr-ODESSA method. The peaks associated with the ortho/meta positions of the outer rings indeed exhibit, in addition, a dispersion at 10 to 100 ms, depending on temperature, which we associate with the π-flips of the outer rings. The rate constant for this process at 25°C is 6.5 s^{-1} and its activation energy is estimated at 62 kJ/mol. No dispersion that could be related to π-flips of the inner rings was observed in the tr-ODESSA results. An upper limit to the rate of this process can be set on the basis of the measured rate for spin diffusion. At room temperature this is more than two orders of magnitude slower than the π-flip rate of the outer rings. We also briefly report on some deuterium T_1 and 2-D-exchange experiments on the lower homologues of the polyphenyl ether series.

1 Introduction

The dynamics of phenyl and phenylene rings in a variety of compounds has, in recent years, been the subject of extensive investigations, using in particular deuterium and carbon-13 nuclear magnetic resonance (NMR). The systems studied range from well-ordered molecular crystals [1] and amorphous polymers [2]

to complex proteins [3]. Most often the dynamics involve degenerate π-flips that do not change the molecular structure. In proteins, such motions have been detected even in structures where the packing forces are expected to prevent them from taking place, and it has been claimed that they proceed in concert with an overall "breathing" motion of the molecules. In polymers, ring flips are believed to be related to their macroscopic properties, in particular to the dissipation of mechanical impact energy [2].

The lower-molecular-weight homologues of the phenyl-O(-phenyl-O)$_n$-phenyl series may be considered as the building blocks of polymers and co-polymers containing fragments of polyphenyl ether chains. They may, therefore, serve as model compounds to investigate phenyl flips in such systems, and on the other hand, they may serve as ideal model compounds for developing methodologies to study motions in solids, particularly in the field of dynamic NMR. The first homologue in this series ($n = 0$, diphenyl ether) melts just above room temperature and has so far not been studied in the solid state. The second homologue ($n = 1$, diphenoxy benzene) forms well-defined crystals with the molecules occupying sites of inversion symmetry. The ring-flip dynamics in this compound was studied in powder samples by carbon-13 magic-angle spinning (MAS) NMR [4] and by the time-reverse one-dimensional exchange spectroscopy by side-band alternation (tr-ODESSA) polarization transfer method [5]. The motion of the two types of rings was found to be uncorrelated with the outer rings flipping much faster than the inner one.
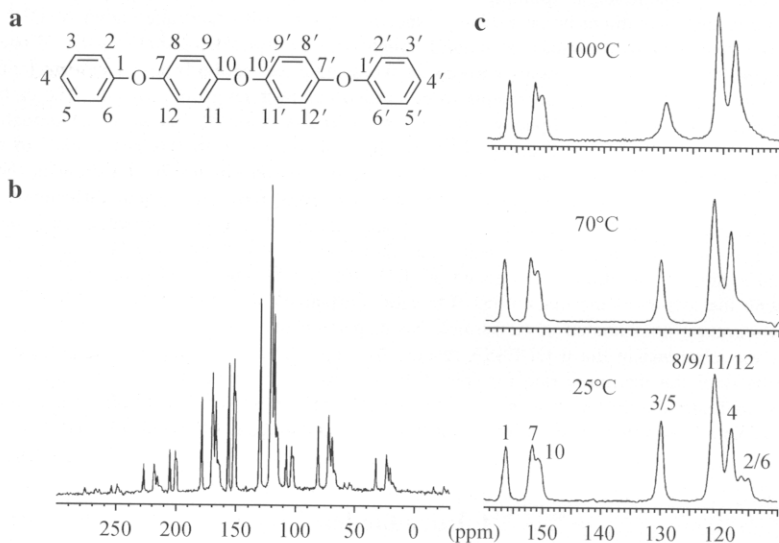

Fig. 1. a Structural formula of DPDPE and the numbering system used to label the carbons. **b** 100.5 MHz carbon-13 MAS spectrum of DPDPE recorded at 25°C with a spinning frequency of 4.9 kHz, 1 ms cross polarization (CP) contact time, 600 s recycle time, and 32 scans. **c** Expanded spectra of the center-band signals at three different temperatures, as indicated. The 25°C spectrum also contains the peak assignment, as explained in the text.

In the present work, we extend the study to the next homologue ($n = 2$) 4,4'-diphenoxydiphenyl ether; in the following, abbreviated to DPDPE (Fig. 1a). We find that in the temperature range of 25 to 100°C the outer rings in this compound undergo measurable π-flips, while the inner ones are static on the NMR time scale. The DPDPE used was a powder sample, which in the MAS experiments gives only partially resolved spectra. Nevertheless, by using the tr-ODESSA experiment, we were able to determine the flipping rate of the outer rings and set an upper limit to that of the inner ones. The results demonstrate the power of the carbon-13 tr-ODESSA method. For comparison we also present preliminary deuterium T_1 and 2-D-exchange experiments on some specifically deuterated, lower homologues of the polyphenyl ether series.

2 Experimental

DPDPE was prepared by Ullmann coupling of potassium phenolate with 4,4'-dibromodiphenyl ether [6]. The latter starting material was prepared from diphenyl ether according to the procedure described in [7]. Potassium phenolate was prepared by heating phenol (7.05 g) under stirring with KOH (3.5 g) until all the water was removed. The Ullmann coupling was effected by adding to the above mixture, 8.4 g of 4,4'-dibromodiphenyl ether and 250 mg of Cu-Bronze, and heating the stirred blend to 230°C for three hours. The resulting DPDPE was purified by bulb-tube distillation at 10^{-1} torr, followed by recrystallization from EtOH. TLC: Silica, CH_2Cl_2/n-hexane 1:1, one spot. $m_z = 354$, m.p. = 109–110°C. An attempt was made to grow single crystals of DPDPE from the melt by slow cooling. At high temperatures, a transparent crystal was obtained which, however, shattered and pulverized on cooling, apparently due to a phase transformation. No crystal structure of the compound is available. The X-ray diffraction pattern of a powder sample obtained by crystallization from ethanol showed well-defined peaks, indicating the material is crystalline rather than amorphous. In the diffractogram, we found a $1/n$ sequence of peaks corresponding to a d-spacing of 20.3 Å. This value is approximately the length of the DPDPE molecule, suggesting a lamellar structure with the molecules stacking perpendicular to the plane.

The carbon-13 NMR measurements were made on a Varian Unity 400 spectrometer, operating at 100.5 MHz. The T_1 deuterium measurements were carried out on a Tecmag modified CXP 300 Bruker spectrometer at 46.07 MHz, while the 2-D deuterium exchange experiments were performed on CMX Infinity 500 at 75.5 MHz. The dynamic measurements were carried out using the tr-ODESSA experiment. This method is a type of 1-D MAS polarization transfer experiment that is particularly suitable for exchange between congruent nuclei. The dynamics is monitored via the decay of the main and/or of the spinning side-band intensities as a function of a variable mixing time, τ_m. The details of the experiment are as outlined in [5]. Experimental parameters are given in the legends of the relevant figures.

3 Results and Discussion

3.1 Carbon-13 CPMAS Spectra: Peak Assignments and T_1 Measurements

A room-temperature carbon-13 MAS NMR spectrum of DPDPE at natural isotopic abundance is shown in Fig. 1b. Expanded spectra of the center peaks at different temperatures are shown in Fig. 1c, with our assignments indicated. This assignment was based on the solution NMR spectrum of DPDPE (which in turn was interpreted with the help of a spectrum calculated using carbon-13 chemical shift additivity rules) and on comparison with the MAS spectrum of the $n = 1$ homologue, diphenoxy benzene [5]. Table 1 contains the calculated and experimental solution chemical shift values, together with those for the MAS spectrum of the solid sample.

Although, as indicated in the experimental section, DPDPE is crystalline, its crystal structure and molecular conformation in the solid state are not known. However, on the basis of the molecular structure and the MAS spectrum of the compound, we shall tentatively assume that the molecule preserves a kind of two-fold symmetry also in the crystal, so that one half of the carbons are congruent to a corresponding second half (see, however, the comment at the end of this section). We accordingly have labeled the atoms by unprimed and corresponding primed numbers, as shown in Fig. 1a. In the following, we refer just to the unprimed set of numbers meaning, however, both.

The three oxygen-bonded carbons 1, 7 and 10, are readily identified in the MAS spectrum (Fig. 1c) by comparison with the solution NMR results. These peaks are not affected by π-flips of either the center or the end phenyl rings. Peak 4 was identified by comparison with the MAS spectrum of diphenoxy benzene. This peak too will not be affected by π-flips of the (outer) rings. The

Table 1. Carbon-13 isotropic chemical shift values (relative to TMS) of DPDPE, in solution (calculated and experimental) and in the solid state.

| Carbon no. [a] | Liquid | | Solid |
	Calculated [b]	Experimental [c]	MAS [d]
1	156.6	158.9	156
7	151.1	154.3	152
10	150.6	153.6	150
2/6	118.9	119.3	115/116
3/5	129.4	130.8	130
4	123.1	124.1	118
8/9/11/12	120.1	120.9/121.6	120/121

[a] The carbon numbering is given in Fig. 1a.
[b] The calculated values were computed using the ACD/^{13}C spectrum generator.
[c] Chemical shifts were measured in a CDCl$_3$ solution at room temperature.
[d] Chemical shifts were determined from the room-temperature MAS spectrum. The width of these peaks is approximately 1 ppm.

peaks due to the ortho and meta carbons of the inner rings 8, 9, 11 and 12, are not resolved (although a shoulder is clearly seen). An estimate of the anisotropic chemical shift tensors of these carbons, on the basis of an analysis of their spinning side-band intensities [8], gave principal values $\delta_{11} = 184.3$, $\delta_{22} = 142.8$, and $\delta_{33} = 33.2$ ppm, relative to TMS. These values are very close to those of static aromatic carbons in similar systems [9], indicating that the inner rings are not undergoing fast flips on the NMR time scale. As we shall see below, they are in fact static even on a much slower time scale.

The peaks assigned as carbons 2 and 6 in the outer rings are resolved (although we cannot tell them apart), while the peaks due to carbons 3 and 5 are not. The latter and its associated side bands are well separated from the other peaks and are thus suitable for tr-ODESSA experiments. An analysis of the spinning side-band intensities of this peak yields a very similar chemical shift tensor as for the 8, 9, 11, 12 peak with components, $\delta_{11} = 224.1$, $\delta_{22} = 136.6$, and $\delta_{33} = 29.3$ ppm. These results indicate that, at room temperature, the outer rings are also in the slow dynamic NMR regime, however, as discussed below, they enter the fast dynamic regime on heating.

The longitudinal relaxation times, of the various peaks in the carbon-13 MAS NMR spectrum at 25°C, were measured by inversion-recovery with Torchia's cross polarization (CP) method with phase alternation [10]. Plots of the peak intensities versus the mixing time for three selected signals in the spectrum are shown in Fig. 2. The other peaks exhibit a similar decay pattern. The decays are mono-exponential and the resulting T_1's for the carbons of interest are summarized in Table 2. The T_1 values of all peaks are rather long (~ 6800 s). Note
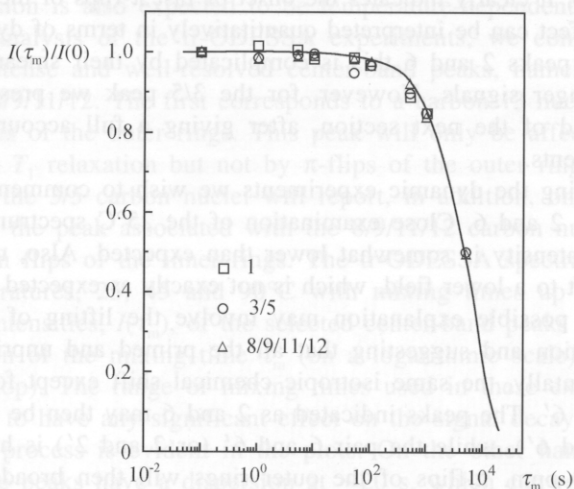

Fig. 2. Results of T_1 measurements at 25°C with the CP inversion recovery method of Torchia with phase alternation [10] and a spinning frequency of 4.9 kHz. The intensities of the labeled peaks (on a linear scale) are plotted against the mixing time (on a logarithmic scale). The solid line is a best fit to a single-exponential decay with $T_1 = 6800$ s.

Table 2. Best-fit parameters to Eq. (1), of the experimental results in Fig. 3.[a]

Carbon no. (C.S./ppm)	Temp. (°C)	A	B	C	k_{ex} (s^{-1})	k_{sd} (s^{-1})	β	T_1[b] (s)
1 (156)	25	—	0.78	0.22	—	0.07	0.60	6750
	45	—	0.85	0.15	—	0.05	0.60	—
3/5 (130)	25	0.19	0.50	0.31	6.5	0.05	0.47	6850
	45	0.15	0.50	0.35	36	0.05	0.56	—
8/9/11/12 (121)	25	—	0.67	0.33	—	0.05	0.58	6730
	45	—	0.77	0.23	—	0.04	0.54	—

[a] The intensities are normalized so that $A + B + C = 1$.
[b] The T_1 results are from independent direct measurements.

that in Fig. 2 the intensities are plotted on a linear scale, while the mixing times are on a logarithmic scale. Such plots exhibit sigmoidal decays (dispersions) at the characteristic times for the relevant dynamic processes, which in Fig. 2 correspond to the T_1's of the various carbons. Thus, on the time scale of up to 100 s the longitudinal relaxation has a negligible effect on the tr-ODESSA measurements. In the next section, where spin exchange experiments are described on much shorter time scales, the T_1 relaxation will, therefore, be ignored.

In Fig. 1c are also shown the center-band carbon-13 MAS spectra obtained at 75 and 100°C. The most conspicuous effect of heating is the broadening of the peaks associated with the ortho/meta carbons of the outer rings. This is apparent from the line shape of the 3/5 peak and the flattening of the peaks due to carbons 2 and 6. It clearly indicates the onset of fast π-flips of the outer rings. The broadening effect can be interpreted quantitatively in terms of dynamic MAS theories [11]. For peaks 2 and 6 this is complicated by their smearing out and overlap with stronger signals. However, for the 3/5 peak we present such an analysis at the end of the next section, after giving a full account of the tr-ODESSA experiments.

Before describing the dynamic experiments we wish to comment on the assignment of peaks 2 and 6. Close examination of the 25°C spectrum in Fig. 1c shows that their intensity is somewhat lower than expected. Also, upon heating they appear to shift to a lower field, which is not exactly as expected for a simple π-flip process. A possible explanation may involve the lifting of the twofold symmetry assumption and suggesting that all the primed and unprimed carbon pairs have, accidentally, the same isotropic chemical shift except for carbons 2 and 2′, and 6 and 6′. The peaks indicated as 2 and 6 may then be identified as 2 and 2′ (or 6 and 6′), while the pair 6 and 6′ (or 2 and 2′) is hidden somewhere around 120 ppm. π-flips of the outer rings will then broaden and shift the "2/6 pair" and the coalescence with the hidden pair will result in intensity enhancement around 118 ppm as indeed observed experimentally at higher temperatures (Fig. 1c). Whatever the correct assignment of the 115/116 ppm (2/6) peaks, it does not affect the analysis of the dynamic effects, which follows.

3.2 Dynamic tr-ODESSA Experiments

The tr-ODESSA method is a version of the polarization-transfer-type experiments in which spin exchange between magnetically equivalent nuclei can be detected under 1-D MAS conditions. During the preparation period the magnetization associated with the various spinning side bands of a set of congruent nuclei are alternately polarized parallel and antiparallel to the external magnetic field. Spin exchange processes, occurring during the mixing time, redistribute the magnetization associated with the spinning side bands, and the rate of these processes is monitored by following the reduction in the intensities of the side-band peaks [5, 12, 13]. The tr-ODESSA experiment provides information about spin exchange between equivalent sites in the crystal, similar to that obtained from the auto cross peaks in MAS 2-D-exchange spectroscopy [14]. It is analogous to the way the usual magnetization transfer experiments [15] between inequivalent sites provide the same information as the hetero cross peaks in 2-D exchange spectra. These 1-D experiments also have the advantage that they do not suffer from poorly defined mixing times, as is the case for short τ_m's in the 2-D exchange experiments [16].

In the DPDPE system, several processes may affect the tr-ODESSA results: (i) longitudinal relaxation, which we have seen is of the order of several thousand seconds; (ii) spin diffusion among the various carbon-13 nuclei (in organic crystals with natural isotopic abundance, this process is usually characterized by exchange times of the order of several seconds, and in general is not dependent on the temperature [17]); and (iii) ring flip dynamics. If the ring flips are faster than the spin diffusion rates, a reduction in the tr-ODESSA peak intensity (dispersion) will occur at a mixing time corresponding to the π-flip life-time, and their dispersion is also expected to be temperature-dependent.

In our analysis of the tr-ODESSA experiments, we concentrated on three relatively intense and well-resolved center-band peaks, namely those numbered 1, 3/5 and 8/9/11/12. The first corresponds to a carbon-13 nucleus situated along the para axes of the outer rings. This peak will only be affected by spin diffusion and by T_1 relaxation but not by π-flips of the outer rings. The peak associated with the 3/5 carbon nuclei will report, in addition, on flips of the outer rings, while the peak associated with the 8/9/11/12 carbon nuclei will yield information on flips of the inner rings. The tr-ODESSA spectra were recorded at three temperatures, 25, 45 and 90°C with mixing times up to 60 s. Figure 3 shows the intensities, $I(\tau_m)$, of the selected center-band peaks (on a linear scale) as a function of the mixing time τ_m (on a logarithmic scale) at 25°C (bottom) and 45°C (top). The range of mixing times used in these experiments was too short for T_1 to have any significant effect on the signal decay and no dispersion due to this process is evident in the plots. On the other hand, it may be seen that all three peaks have a dispersion at ~20 s, which can readily be identified with the spin diffusion process. This interpretation is supported by the observation that the corresponding dispersion times are similar at 25 and 45°C. Finally, we note that the 3/5 peak displays additional dispersion, corresponding to 75 and 13 ms at 25 and 45°C, respectively. We identify these dispersions as due to the
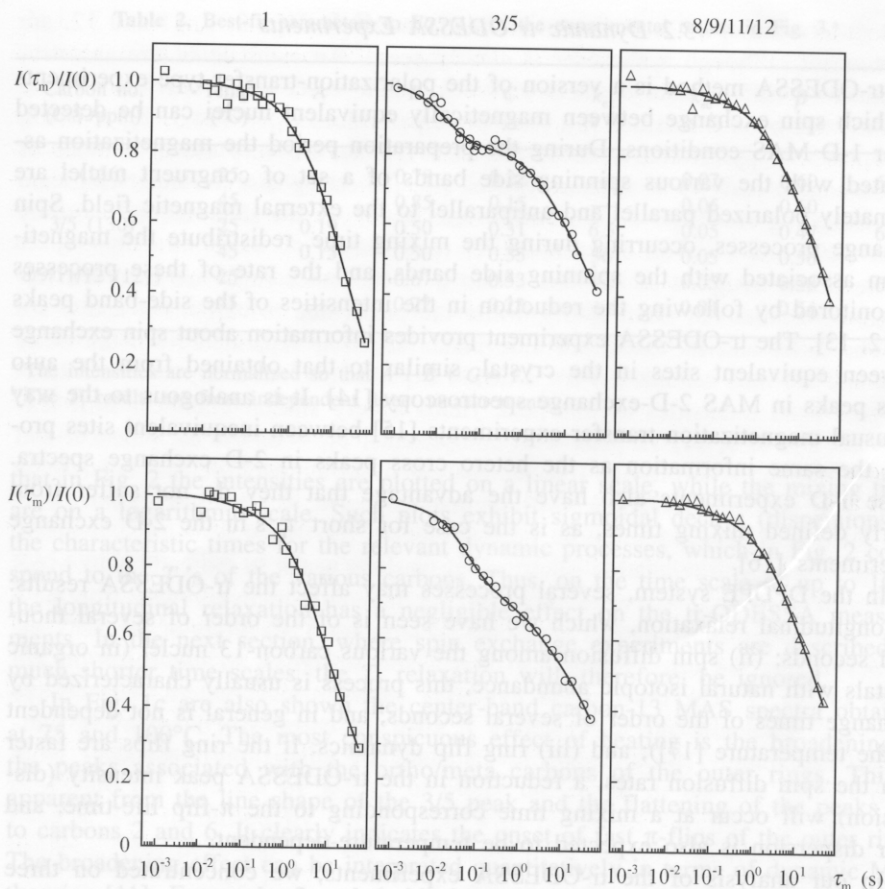
Fig. 3. Results of tr-ODESSA experiments recorded at 25°C (bottom) and 45°C (top) with a spinning frequency of 4.9 kHz. The intensities (on a linear scale) of three selected center peaks, as indicated, are plotted as functions of the mixing time (on a logarithmic scale). The solid lines are best fits to Eq. (1) with the best-fit parameters given in Table 2. Each experimental point is a result of 32 scans, phase-cycled as explained in [5]. A recycle time of 600 s was used, resulting in a total measuring time of about 6 h for each point.

π-flip dynamics of the outer rings. It should be noted that large amplitude fluctuations could also be responsible for the observed dispersions in the 3/5 peak. However, such a motion should affect the tr-ODESSA decay of peak 1 (and 4) contrary to the experimental observation (Fig. 3). Also a π-flip mechanism is consistent with the crystalline nature of DPDPE.

Since the three dynamic processes discussed above, π-flips, spin diffusion and longitudinal relaxation, occur on well-separated time scales, we may analyze the intensities, $I(\tau_m)$, of Fig. 3 in terms of a sum of exponential functions:

$$I(\tau_m) = A\exp(-2k_{ex}\tau_m) + B\exp(-k_{sd}\tau_m)^\beta + C. \tag{1}$$

In this equation, the first term reflects the effect of the ring flip, with k_{ex} representing the rate coefficient for the process [5]. The second term accounts for the effect of spin diffusion. Because the spin diffusion process corresponds to a distribution of rates, a stretched exponential function was used [18], with k_{sd} representing some average spin diffusion rate coefficient, and β, a parameter related to its distribution. The last term in Eq. (1) reflects the effect of T_1 relaxation. It was, however, set to a constant, since during the mixing times used in our experiments, longitudinal relaxation did not contribute significantly to the decay of the peak intensities. The solid lines in Fig. 3 are best fits to Eq. (1), with the best-fit parameters summarized in Table 2. In principle, one could calculate the factor A, associated with the ring flip process from the corresponding carbon-13 chemical shift tensors [14]. Such a calculation yields $A = 0.28$ (instead of 0.19 and 0.15 in Table 2). The discrepancy may partly be due to non-optimal experimental conditions, but it should also be noticed that the calculated value is quite sensitive to the assumed tensor orientation. Thus if we assume a jump angle of 140° (rather than 120°) the calculated value of A reduces to 0.16. We felt, however, that the proposed interpretation is pretty certain and chose to consider it as a free parameter.

Referring to the results in Table 2, we note that k_{sd} is similar for all carbons and essentially independent of the temperature, as expected for spin diffusion. Also, the exponent β is similar to that found for carbon-13 in other organic crystals [19]. On the other hand, the extra dispersion due to ring flips is only found for the 3/5 peak (among those selected for the analysis) and the associated rate coefficient is strongly temperature-dependent, as expected for a thermally activated dynamic process. To evaluate the kinetic parameters of k_{ex} we have used the tr-ODESSA results at 25 and 45°C and combined them with rate constants derived from an analysis of the dynamically broadened MAS spectra at 70 and 100°C (Fig. 1). Specifically, the broadening of the 3/5 peak was analyzed with Floquet's theory as described in [11]. For the calculation we used the chemical shift tensor determined above for the 3/5 peak, with the direction of δ_{33} perpendicular to the aromatic ring and δ_{11} along the C-H bond. The ring flip thus corresponds to reorientation of the chemical shift tensor by ±60° about δ_{33}. The natural line width (full width at half-maximum height, fwhmh) was taken as 105 Hz, which was the width measured for this line at both 0 and 25°C, where the dynamic broadening is negligible. In practice a series of dynamically broadened spectra were calculated for the above parameters with $\nu_R = 4.9$ kHz and a wide range of k_{ex} values. The fwhmh of the center peak was then measured and plotted as function of the flip rate. Examples of such calculated peaks and the corresponding plot are shown in Fig. 4. As expected, the line width passes through a maximum when k_{ex} is of the order of magnitude of the chemical shift anisotropy. The experimental line widths at 70 and 100°C clearly correspond to the broadening branch of the curve. From their values the k_{ex}'s at these temperatures could readily be determined. The results are shown in terms of an Arrhenius plot in Fig. 5, together with those obtained from the tr-ODESSA experiments. They yield an activation energy of 62 kJ/mol and a pre-exponential factor of 10^{13} s^{-1}.
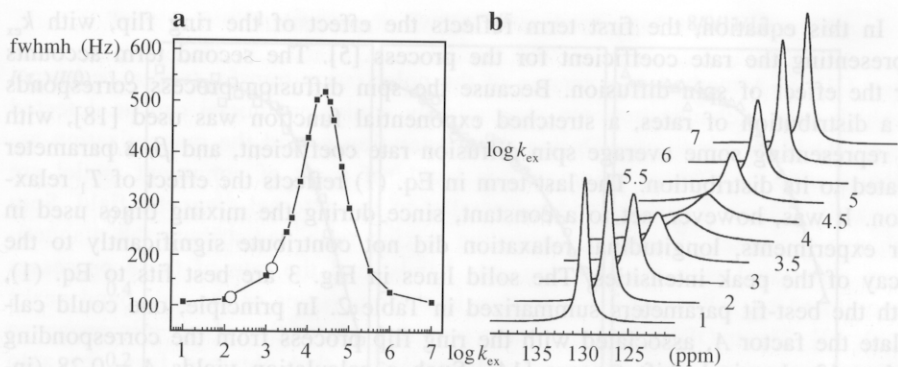
Fig. 4. a A plot of the fwhmh of the 3/5 center peak as determined from simulated spectra of the type shown on the right. Solid squares are calculated values; the two open circles are the experimental points at 70 and 100°C. **b** Simulated dynamic MAS line shapes of the DPDPE 3/5 center peak for different flipping rates of the outer ring, as indicated. The parameters used are indicated in the text. k_{ex} is in s^{-1}.

The flip rate of the outer rings in DPDPE is similar to that for the outer rings in diphenoxy benzene [4, 5]. However, the situation for the inner rings is quite different. In the latter compound, flipping of the inner ring was detected by tr-ODESSA at rates slower by about one order of magnitude than those of the outer ones. In DPDPE, no dynamic effects were detected on the carbon-13 signals of the inner ring (carbons 8/9/11/12). Any flipping of these rings at temperatures
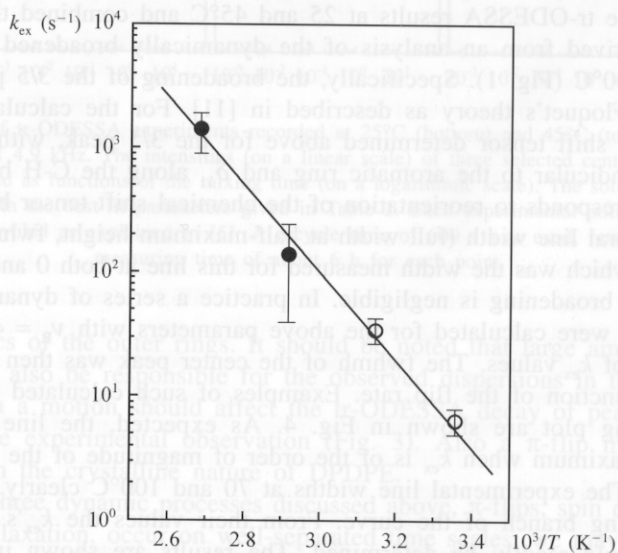

Fig. 5. Arrhenius plot of k_{ex}. Open symbols correspond to points obtained from the tr-ODESSA results at 25 and 45°C (Fig. 3); solid symbols are obtained from the MAS spectra at 70 and 100°C (see Fig. 1c).

below 45°C must, therefore, be slower than the spin diffusion rate ($\sim$0.05 s^{-1}), i.e., at least two orders of magnitude slower than that for the outer rings. The flipping rate of the outer rings at 90°C is too fast to measure by tr-ODESSA. This is manifested in the fast decay of the 3/5 peak, which results in a poor signal-to-noise ratio. The decay rate of peak 1 at this temperature is essentially the same as that measured at 25 and 45°C, as would be expected for a mechanism dominated by spin diffusion. On the other hand, the decay rate of the 8/9/11/12 peak, due to the inner ring carbons, is slightly faster ($\sim$0.1 s^{-1}) than that measured at the lower temperatures ($\sim$0.05 s^{-1}). This may reflect the appearance of inner ring flips at 90°C. From the observed decays, an upper limit of 0.05 s^{-1} can be set for the rate of this process at this temperature.

3.3 Deuterium NMR Results

The long T_1's measured for the carbon-13 nuclei in DPDPE clearly reflect the slow molecular mobilities in this compound. For parallel deuterium NMR studies of the polyphenyl ether series, we prepared DPDPE selectively deuterated in the inner (DPDPE-d$_8$) and outer (DPDPE-d$_{10}$) rings, diphenoxy benzene (DPB) deuterated in the inner (DPB-d$_4$) and outer (DPB-d$_{10}$) rings, as well as perdeuterated diphenyl ether (DPE-d$_{10}$). The measured deuterium T_1's in all these compounds ranged from 130 to 1220 s, except for that of DPB-d$_4$, for which T_1 was
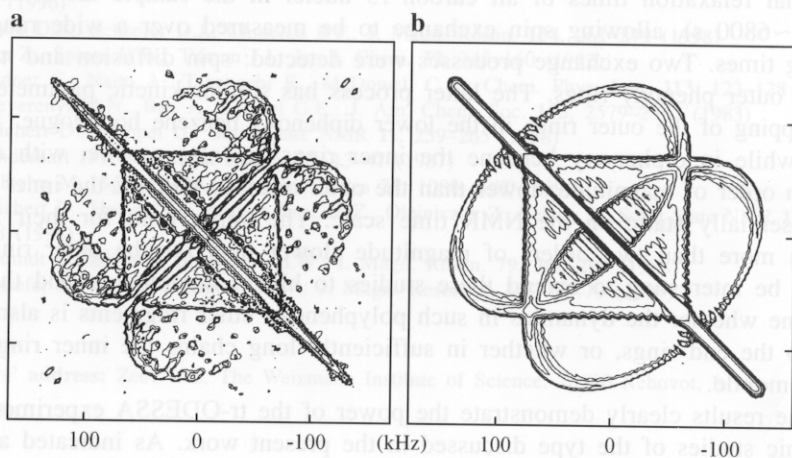

Fig. 6. Deuterium 2-D exchange spectra of DPB-d$_4$. **a** Experimental spectrum (75.5 MHz) recorded at 55°C with a mixing time of 0.1 s and the five-pulse sequence [21]. Other experimental details: 3 µs dwell time in both t_1 and t_2, corresponding to 333 kHz sweep width in both dimensions; 20 and 30 µs echo delays in t_1 and t_2, respectively. Number of data points acquired, 40 in t_1 and 64 in t_2, zero-filled to 128 by 128 before Fourier transformation; recycle time 2 s; two sets (Zeeman and quadrupole order) of 512 scans each were accumulated for each t_1 value; π/2 pulse width 2 µs. **b** Calculated spectrum for complete exchange, assuming ±60° flips of the C-D bonds and an axially symmetric quadrupole tensor with a principal component of 132 kHz.

0.4 s. We are unable to explain the abnormally short deuterium T_1 of the inner ring deuterons in the latter compound. We first suspected paramagnetic impurities, remaining from the deuteration process. However, the same T_1 was also measured in a DPB-d_4 sample that had undergone repeated chromatographic purification. A possible mechanism for the short T_1 could be fast low-angle librations, which for some reason are specific to the center ring of DPB. However, we have no independent results to support this hypothesis. In particular the ^{13}C T_1 of the inner-ring carbons do not show a similar anomaly. On the other hand, the short deuterium T_1 of this sample made it feasible to perform a 2-D-exchange experiment [20, 21]. Recall that in diphenoxy benzene the inner ring undergoes slow flips [5], which should be detectable by deuterium 2-D-exchange NMR spectroscopy. The results of such an experiment are shown in Fig. 6a. The experimental 2-D-exchange deuterium NMR spectrum (75.5 MHz) was recorded at 55°C with a mixing time of 0.1 s. Elliptical exchange ridges, corresponding to two-site flips of the C-D bonds by $\pm 60°$, are clearly observed (see calculated spectrum in Fig. 6b). This confirms the earlier conclusion derived from the tr-ODESSA experiment [5].

4 Summary and Conclusions

We have performed carbon-13 tr-ODESSA experiments in order to measure spin exchange processes in the solid oligomer 4,4'-diphenoxydiphenyl ether. The longitudinal relaxation times of all carbon-13 nuclei in the sample are extremely long (~ 6800 s), allowing spin exchange to be measured over a wide range of mixing times. Two exchange processes were detected: spin diffusion and π-flips of the outer phenoxy rings. The latter process has similar kinetic parameters as the flipping of the outer rings in the lower diphenoxy benzene homologue. However, while in diphenoxy benzene the inner rings are also mobile, with a flip rate an order of magnitude slower than the outer ones, in DPDPE the inner rings are essentially static on the NMR time scale. The upper limit for their π-flip rate is more than two orders of magnitude slower than for the outer rings. It would be interesting to extend these studies to higher homologues and thereby examine whether the dynamics in such polyphenoxy ether fragments is also limited to the end rings, or whether in sufficiently long chains the inner rings become mobile.

The results clearly demonstrate the power of the tr-ODESSA experiment for dynamic studies of the type discussed in the present work. As indicated above, tr-ODESSA is a 1-D version of the rotor-synchronized 2-D MAS exchange experiment [14]. The low intrinsic sensitivity of carbon-13 in natural abundance and the extremely long T_1's of the DPDPE carbons render the 2-D version impractical. Even a single tr-ODESSA run (with 24 mixing times) took about one week of measuring time; by comparison a 2-D experiment with the same number of mixing time points would require about six months of continuous measurements.

Acknowledgements

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