Phenylene Ring Dynamics in 1,4-diphenoxybenzene

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The crystal structure for 1,4-diphenoxybenzene has been determined; M = 262.3, space group $P2_1/c$, a = 5.856(2), b = 7.822(2), c = 15.422(4) Å, β = 95.24(2), U = 703.7 Å, Z = 2. Molecules of 1,4-diphenoxybenzene adopt a structure with *trans* coplanar terminal rings and the central benzene ring is orthogonal to these giving torsion angles close to 90°. Chemical shift inequivalences are seen in the ^{13}C CPMAS NMR spectra which can be attributed to an electric-field effect from the electric dipole of the ether group. Using these chemically inequivalent resonances the phenylene ring dynamics have been investigated. The terminal phenyl rings were found to undergo π 'flips' with an activation energy of 59.1 kJ mol^{-1}. Indirect estimates of the 'flip rate' for the central ring show that it is flips much more slowly than the terminal rings.

Phenylene ring motions are found in a variety of macromolecular compounds ranging from polymers [1–4] to proteins,[5–7] The case of protein ring motion within the mass of a globular protein, seemingly prevented by Van der Waals interactions, illustrates the need to take into account the dynamic aspects of the structure when considering its function.[8] However, it should be stressed that phenylene ring dynamics are unlikely to play a direct functional role. Most work in the polymer field has highlighted the relationship between the polymer dynamics and their mechanical properties, in particular their impact strength.[9,10] The precise nature of the link is not clear, but two views can be identified. First, it has been proposed that the ring motion acts in a direct manner to dissipate the mechanical energy,[10] and secondly, the ring motion is believed to be only an indicator of the mechanical relaxation process, perhaps showing the presence of free volume which allows movement of the polymer chains with respect to one another thereby dissipating the mechanical energy.[11]

When van der Waals contacts prevent ring motion it is apparent that a relaxation must occur in the three-dimensional structure if a flip is to take place, that is, the ring motion is concerted with, perhaps, a breathing motion of the lattice. A model for phenylene ring flips has been proposed for polycarbonate based on this idea, and the corollary of this is that if the lattice is rigid then ring motion will be restricted.[10] Computer simulations of the phenylene ring flips in a much simplified model polymer system support the proposed relationship between ring motion and lattice deformations.[12] For an aryl polymer, such as polycarbonate or (polyether) ether ketone, where many phenylene rings are in a polymer chain, an additional question is whether the ring flips themselves occur in a co-operative manner. The macromolecular compounds are, to a certain extent, a special case because the ring dynamics can be accommodated within the many degrees of freedom of the free-energy surface. Consequently, in order to explore the constraints on phenylene ring motion and the possibility of co-operative 'flips' in polyaryl systems, it is of particular interest to observe phenylene-ring motion in the crystalline phases of small molecules of known structure. Despite the need for efficient packing to minimise the free energy of a molecular solid by maximising the intermolecular dispersion forces, phenylene-ring motion is not uncommon. Recently ring flips have been observed in penicillin derivatives [13] and in one crystal form of 4,4'-isopropylidinebis(diphenyl carbonate).[14] From an examination of these and related systems it will be possible to build up a picture of the way intermolecular potentials influence ring dynamics.

In this paper the phenylene ring motions in 1,4-diphenoxybenzene as derived by ^{13}C MAS NMR spectroscopy are reported and discussed in the light of the crystal structure. Of particular importance is that 1,4-diphenoxybenzene is one of the simplest fragments which can be used to model polymers containing aryl ethers such as poly(phenylene oxide) and (polyether) ether ketone (PEEK). For this reason the structure in terms of crystal packing and torsional angles is of note.

Experimental

Solid-state NMR Spectroscopy.—Solid-state NMR experiments were carried out using a Bruker MSL 200 NMR spectrometer operating at 50.32 MHz for ^{13}C. High-resolution spectra were obtained by using magic angle spinning and high power proton decoupling while the sensitivity was enhanced by cross polarisation through a spin–lock pulse sequence with a contact time of 1 ms.[15] Typically MAS speeds of 4 kHz were used except for the slow-spinning experiments when speeds of 1–2 kHz were necessary. The chemical-shift tensors were derived from the spinning sideband intensities in the slow-spinning spectra by computer simulation of the MAS spectrum using a SIMPLEX routine.[16,17] A combination of lineshape analysis and magnetisation transfer experiments using the one-dimensional analogue of the two-dimensional chemical exchange method [18,19] were employed to determine the rate of the phenylene-ring motion.

Crystal Structure Determination.—Single crystal X-ray diffraction data were collected on a Nicolet R3m diffractometer with Cu-K_α radiation using ω-scans. 951 independent reflections were measured (2θ < 116) of which 923 had $F_o > 3\sigma F_o$ and were considered to be observed. The data were corrected for Lorentz and polarisation factors; no absorption correction was applied. The structure was solved by direct methods with the non-hydrogen atoms refined anisotropically. Idealised hydrogen positions were used, with C–H = 0.96 Å, they were assigned isotropic thermal parameters and allowed to ride on their parent carbon atoms. Refinement was by block-cascade, full-matrix least-squares method to R = 0.045, R_w = 0.070. The

Table 1. Atom co-ordinates with estimated standard deviations in parentheses.

	Atom co-ordinates × 10^4		
Atom	*x*	*y*	*z*
C(1)	3 668(3)	1 408(2)	3 445(1)
C(2)	3 605(4)	301(3)	2 747(2)
C(3)	1 815(4)	−802(4)	2 580(2)
C(4)	75(4)	−838(3)	3 126(2)
C(5)	99(3)	271(3)	3 816(1)
C(6)	1 917(3)	1 389(2)	3 972(1)
O(6)	1 781(3)	2 464(2)	4 674(1)
C(7)	3 434(3)	3 727(2)	4 826(1)
C(8)	5 415(4)	3 384(3)	5 338(2)
C(9)	7 003(3)	4 678(3)	5 515(1)

Table 2. Bond lengths with esds in parentheses.

Bond	Length/Å	Bond	Length/Å
C(1)–C(2)	1.380(3)	C(1)–C(6)	1.365(3)
C(2)–C(3)	1.364(3)	C(3)–C(4)	1.380(4)
C(4)–C(5)	1.373(3)	C(5)–C(6)	1.382(3)
C(6)–O(6)	1.379(2)	O(6)–C(7)	1.388(2)
C(7)–C(8)	1.368(3)	C(7)–C(9′)	1.368(3)
C(8)–C(9)	1.385(3)	C(9)–C(7′)	1.368(3)

Table 3. Bond angles with esds in parentheses.

Bonds	Angle/°	Bonds	Angle/°
C(2)–C(1)–C(6)	119.3(2)	C(1)–C(2)–C(3)	120.6(2)
C(2)–C(3)–C(4)	119.7(2)	C(3)–C(4)–C(5)	120.3(2)
C(4)–C(5)–C(6)	119.2(2)	C(1)–C(6)–C(5)	120.8(2)
C(1)–C(6)–O(6)	124.1(2)	C(5)–C(6)–O(6)	115.0(2)
C(6)–O(6)–C(7)	118.5(2)	O(6)–C(7)–C(8)	119.9(2)
O(6)–C(7)–C(9′)	118.7(2)	C(8)–C(7)–C(9′)	121.3(2)
C(7)–C(8)–C(9)	119.3(2)	C(8)–C(9)–C(7′)	119.4(2)

maximum residual electron densities in the final Δ/*F* map were 0.16 and −0.14 e Å respectively. The mean and maximum shift/error in the final refinement were 0.001 and 0.003, respectively.

Results and Discussion

Crystal data for 1,4-diphenoxybenzene are; $M = 262.3$, space group $P2_1/c$, $a = 5.856(2)$, $b = 7.822(2)$, $c = 15.422(4)$ Å, $\beta = 95.24(2)$, $U = 703.7$ Å, $Z = 2$, and $D_c = 1.24$ g cm^{-3}. A view of the molecular structure is shown in Figure 1, the main feature of which is the coplanar arrangement of the terminal rings and the orthogonal central benzene ring. This structure is not the lowest-energy conformation for the isolated molecule. STO-3G[20] and semiempirical calculations[21] suggest that a skewed conformation is roughly 4 kJ mol^{-1} lower in energy. However, such an orthogonal conformation might allow more efficient packing in the crystal and the larger resulting intermolecular interactions could favour this conformation. Atom co-ordinates are shown in Table 1 with the hydrogen co-ordinates in Table 6 and the bond lengths in Table 2. Bond angles and the principal torsion angles are listed in Tables 3 and 4 respectively. The anisotropic temperature factors and hydrogen-atom co-ordinates have been deposited at the Cambridge Crystallographic Data Centre.* Despite the adoption of the orthogonal conformation the density of the packing is not very high, tending to suggest that this conformation is favoured because it reduces unfavourable intermolecular contacts rather than giving particularly efficient packing.

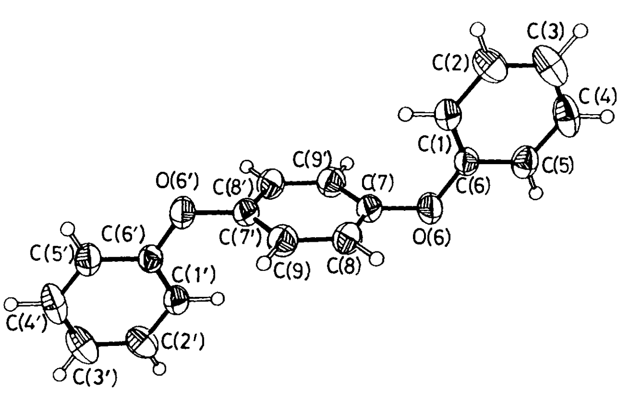

Figure 1. Crystal conformation of 1,4-diphenoxybenzene.

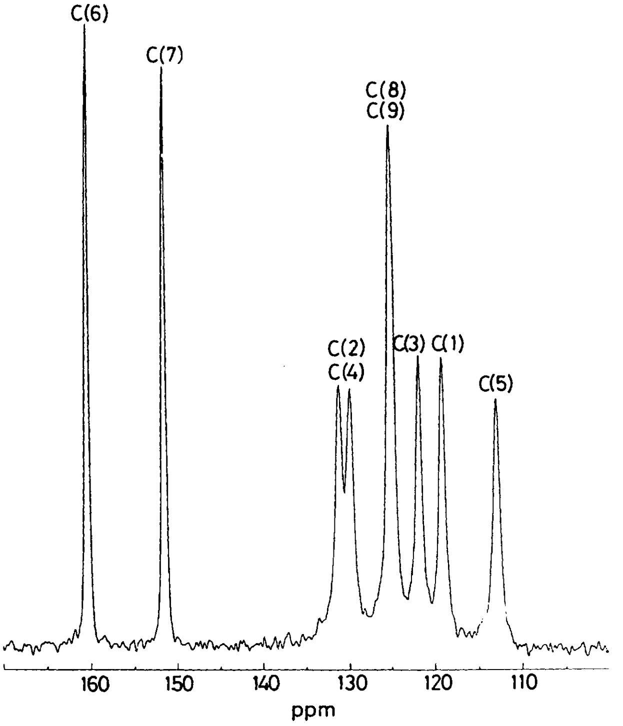

Figure 2. 50.32 MHz ^{13}C CPMAS NMR spectrum of 1,4-diphenoxy benzene together with the resonance assignments.

A significant feature of the ^{13}C CPMAS NMR spectrum shown in Figure 2 is the chemical inequivalence of only one set of resonances from the carbons C(1) and C(5) *ortho* to the ether oxygen, namely those at 112.8 and 119.0 ppm. Assignment of these resonances to the phenoxy groups is straightforward, based on the substituent effects of the phenoxy group. Additionally, a splitting is seen of the *meta* carbons [C(2) and C(4)] in the phenoxy ring at 130 ppm. In principle, the

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* For details of the CCDC deposition scheme, see 'Instructions for Authors (1990).' *J. Chem. Soc., Perkin Trans. 2*, 1990, issue 1.

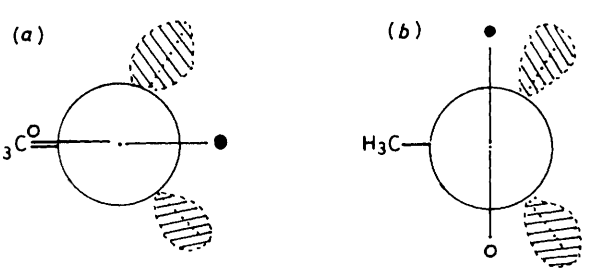

Figure 3. Projections along the C–O bond illustrating the two extreme conformations of the oxygen non-bonding orbitals.

Table 4. Torsion angles with esds in parentheses.

Bonds	Torsion angle/°	Bonds	Torsion angle/°
C(6)–C(1)–C(2)–C(3)	0.1(3)	C(2)–C(1)–C(6)–C(5)	0.4(3)
C(2)–C(1)–C(6)–O(6)	−178.5(2)	C(1)–C(2)–C(3)–C(4)	−1.5(4)
C(2)–C(3)–C(4)–C(5)	2.3(4)	C(3)–C(4)–C(5)–C(6)	−1.0(3)
C(4)–C(5)–C(6)–C(1)	0.4(3)	C(4)–C(5)–C(6)–O(6)	179.4(2)
C(1)–C(6)–O(6)–C(7)	4.7(3)	C(5)–C(6)–O(6)–C(7)	−174.3(2)
C(6)–O(6)–C(7)–C(8)	−89.2(2)	C(6)–O(6)–C(7)–C(9′)	93.4(2)
O(6)–C(7)–C(8)–C(9)	−177.2(2)	C(9′)–C(7)–C(8)–C(9)	0.2(4)
C(7)–C(8)–C(9)–C(7′)	−0.2(4)		

Table 5. Chemical shift tensor components[a] for 1,4-diphenoxybenzene.

Resonance	σ_{11}	σ_{22} (ppm)	σ_{33}	σ_{iso} (ppm)	χ^2	Q[b]
C(5)	183.5	144.1	10.4	112.8	0.10	0.99
C(1)	194.9	141.1	21.2	119.05	0.49	0.92
C(3)	217.8	130.6	16.7	121.66	0.83	0.84
C(8), C(9)	204.6	144.2	26.06	124.96	0.15	0.98
C(2)	223.1	152.8	16.3	131.0	0.25	0.97
C(7)	242.9	141.1	70.8	151.6	0.43	0.93
C(6)	242.0	166.2	73.3	160.5	0.54	0.91

[a] Experimental standard deviation = 0.03. [b] Goodness-of-fit (ref. 27).

differences in chemical shift observed within the sets of *ortho* and *meta* resonances can be used to look at the structure in more detail. However, the interpretation and calculation of chemical shift inequivalences is difficult and remains a major obstacle to the derivation of structural information by solid-state NMR spectroscopy. Despite this, an examination of a range of compounds with phenyl ether bonds provides strong evidence that the splittings in this case arise from the orientation of the phenyl rings with respect to the ether oxygen non-bonding orbitals. Consequently, the splittings can be calculated by the model of an electric-field induced shift.[22,23] A qualitative description follows with reference to Figure 3 which shows the possible orientations of the oxygen non-bonding orbitals with respect to the *ortho* carbons in dimethoxybenze. The maximum observed splitting, 6.2 ppm, of the more shielded resonances is almost identical with that observed for 1,4-dimethoxybenzene where the crystal structure shows coplanarity of the phenyl and methoxy groups. For 1,4-dimethoxybenzene this means the oxygen non-bonding orbitals point towards one *ortho* carbon [C(5)] and away from the other [C(1)]. Exactly the same orientation is evident, from the crystal structure, for the terminal phenoxy groups in 1,4-diphenoxybenzene and in agreement with the electric field model a splitting of *ca.* 6.2 ppm is seen. Moreover, for the central benzene ring where the oxygen non-bonding orbitals are symmetrically disposed towards the *ortho* carbons of the central benzene ring, a negligible shift is expected and is observed. Thus the explanation of the *ortho* carbon chemical shift differences in terms of an electric field effect from neighbouring ether groups does seem to be valid. Hence the differential shifts observed for these carbons in polymeric systems can be used to derive the phenoxy–phenyl torsion angle. For example in poly(phenylene oxide) where a splitting of 3.2 ppm is seem for the crystalline phase a qualitative description is that of skewed phenyl rings; moreover, we can estimate a torsion angle of about 30–40°. In order to shed more light on the mechanism causing the electric field shift the chemical shift tensors were determined (Table 5). This can often be fruitful because not infrequently small changes in the isotropic chemical shift disguise more marked changes in the chemical shift tensor components; however, in this case the differences between the two sets of chemical shift tensors is little more than in the isotropic shift. The largest differences are seen for σ_{11}, and σ_{33} components and are equal to *ca.* 11 ppm. Thus although the electric-field shift does act in an anisotropic manner the effect is not marked.

As well as giving structural information, the difference in chemical shift seen for the *ortho* carbons is extremely important as it means that the isotropic ^{13}C resonance can be used to investigate the phenyl ring dynamics. This is demonstrated by the temperature dependence of the ^{13}C CPMAS NMR spectrum, Figure 4. In the terminal ring both the chemically inequivalent *ortho* and *meta* carbons show classical two-site exchange lineshape changes with increasing temperature of broadening, coalescence and then narrowing. In view of the simple two-site character of the exchange process the rate was derived from the variable temperature spectra by a comparison with computer simulated spectra. Extension of the measurement of the rate into the slow exchange region was achieved using the one-dimensional chemical exchange pulse sequence. An Arrenhius plot of the derived exchange rates for the two sets of resonances is shown in Figure 5. From the observation of the exchange of resonances either side of the phenyl ring it is not possible to deduce the type of ring motion; both a π flip and continuous rotation are consistent with the data. Normally one would turn to the anisotropic component, namely the chemical shift tensor, to differentiate between these possibilities. However, in this case the ring does not move sufficiently fast to average the chemical shift tensor before the melting point is reached.

Evidence regarding the nature of the ring dynamics is provided by the X-ray crystal structure where the observation of discrete positions for the phenyl rings indicates that they are not free rotors; hence the rings are flipping. Furthermore, close examination of the thermal parameters shows no evidence for additional motions such as torsional oscillations about the C–O axis or 'wagging' out of the plane, thus indicating a steep-sided intermolecular potential in the lattice. It is somewhat difficult to compare this result with previous work in polymers since faster ring dynamics have in general been studied and in such systems torsional oscillations are found to increase in amplitude with the flipping rate. On the other hand ring flips in a few biological molecules have been demonstrated to occur with minimal additional motions.[24] Some evidence for a restricted 'wagging' of the ring attached to the carbonate is seen in 4,4′-isopropylidene bis-(diphenyl carbonate)[14] rather than torsional oscillations while for phenoxy penicillin K again there is no evidence for additional motions.[25] It is thus apparent that clear differences are seen between ring motion in crystalline phases and amorphous polymers, not only in the homogeneity of the ring flip rate but also in the presence of other motions.

A peculiar Arrhenius plot (Figure 5) is seen for the *meta* resonances of the phenoxy rings which seems to imply a levelling off in the ring 'flip' at higher temperature. In contrast, the plot for the *ortho* phenoxy resonances is linear, enabling an

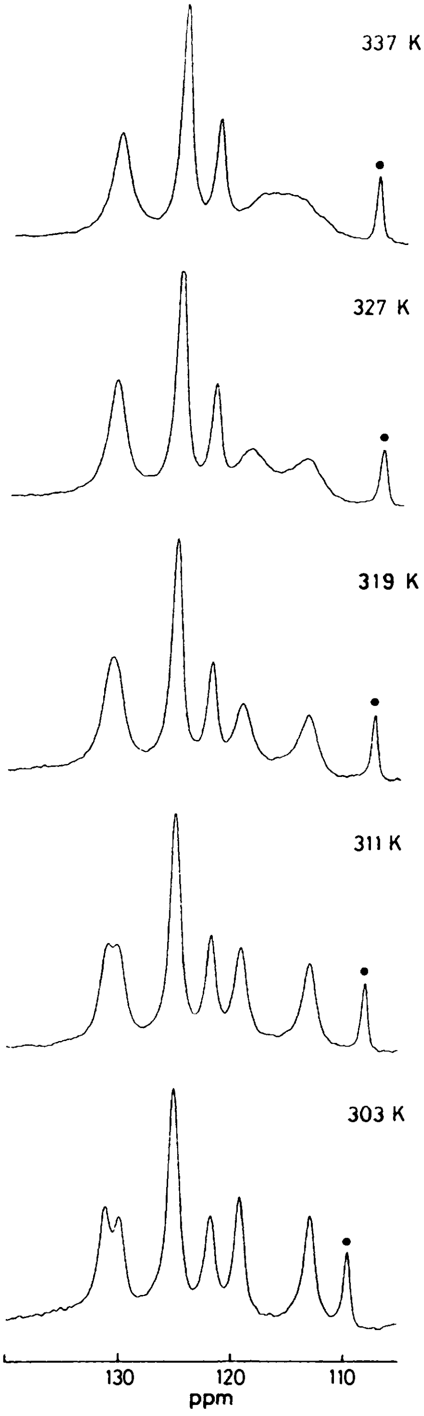

Figure 4. Temperature dependence of the ^{13}C CPMAS NMR spectrum of 1,4-diphenoxybenzene.

activation energy of 59.1 kJ mol^{-1} with a standard error of 5.1 kJ mol^{-1} and a frequency factor of 0.13 × 10^{12}–8.0 × 10^{12} s^{-1} to be derived (Figure 5). The goodness-of-fit was 0.93 for this correlation. The probable explanation for the apparent tailing-off in rate observed for the *meta* carbons is as follows. Above the coalescence temperature the *meta* resonance should continue to narrow to around 25 Hz, hence the levelling-off in the rate implies that the observed linewidth is greater than expected. Broadening of a magic-angle-spinning averaged resonance will occur when a dynamic process is of the same order of magnitude as the spinning speed.[26] Under these circumstances the dynamic process will interfere in the coherent averaging providing the chemical shift tensor is altered by the process. From the *ortho* resonances we know that the flip rate is 0.7 kHz at 340 K, only a factor of four less than the MAS speed; consequently, we would expect some broadening to occur. A similar effect is not seen for the *ortho* resonances simply because of the large natural linewidth of 400 Hz caused by the exchange being close to the coalescence point while the *para* resonances are not broadened because the π flip leaves the chemical-shift tensor unchanged.

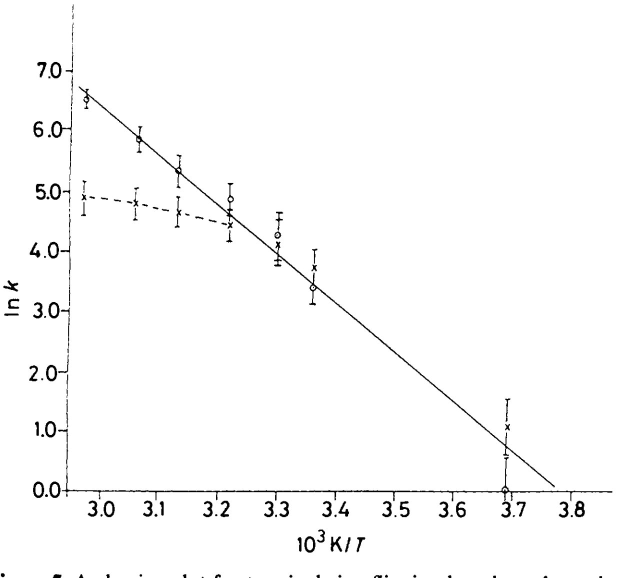

Figure 5. Arrhenius plot for terminal ring flipping based on the *ortho* and *meta* carbons: X = C(2), C(4); ○ = C(1), C(5).

A consequence of the conformation of 1,4-diphenoxybenzene is that the *ortho* resonances for the central ring are equivalent which prevents the direct examination of its ring flip rate by ^{13}C CPMAS NMR. An indirect estimate can be made, however, following the argument indicated for the *meta* resonances. Thus if the central ring is flipping at a similar rate to the phenoxy ring we would expect to see an increase in the linewidth. Indeed given the same 'flip' rate as the phenoxy ring of 0.7 kHz at 340 K the linewidth is expected to increase to around 100 Hz. This is not observed, the linewidth of the *ortho* resonance of the central ring is unchanged from 50 Hz at 260 K up to 340 K. We can therefore be confident that the central ring does not flip at the same rate as the terminal phenoxy rings. Fast π flips over the temperature range studied can be ruled out by the values of δ and η for the chemical-shift tensor. Hence the central ring must flip at a much slower rate than the terminal rings. A concerted π flip of all three rings is therefore not the major dynamic process although it is possible that flipping of the central ring (when it does occur) is concerted with π flips of the terminal rings.

Calculations for isolated molecules indicate that when the ring motion is co-operative the intramolecular activation barrier to flipping is negligible.[20] However, in a rigid crystalline lattice co-operative ring flips will tend to be prevented by large intermolecular potentials.[12] Thus co-operative ring flipping is only possible when the intermolecular potentials are weak. For an isolated molecule of 1,4-diphenoxybenzene we would expect the activation energy for a flip of the central ring to be greater than that of the outer rings and thus at first sight the observed differences in flipping rates is not surprising. Indeed it is of note that many examples of phenylene ring motion involve terminal rings. Yet, central ring motion has been observed in the well-defined crystalline phase of 4,4′-isopropylidenebis(diphenylcarbonate)[14] and moreover this view ignores the significant increase in the activation barrier observed in the solid for the non-concerted terminal ring flip which is only 20 kJ mol^{-1} or so in the isolated molecule but measured in the crystal to be 59.1 kJ mol^{-1}. From a consideration of the packing in the crystal it is apparent that rotation of the terminal and central rings involves significant van der Waals contacts, highlighting the need for lattice deformations to permit ring dynamics. This being so, the absence of co-operative ring flips, or at least a similar flip rate for the central ring becomes more problematic. To provide a more quantitative account of the phenyl ring dynamics in terms of the crystal potentials it is necessary to calculate how the isolated molecule conformational barriers are affected by the close packing in the lattice and then modified by lattice relaxation.

It is of note that for 4,4′-isopropylidenebis(diphenyl carbonate) which exists in two crystalline modifications, one form, with the higher density of 1.308 g cm^{-3}, is immobile while the other form for which ring motion is seen has a density of 1.24 g cm^{-3} *i.e.* very similar to that of 1,4-diphenoxybenzene.[28] The lower density of packing entails a smaller lattice deformation before ring flipping can occur.

Conclusions

The single crystal structure of 1,4-diphenoxybenzene has been determined. Essentially the molecular conformation involves *trans* terminal phenyl rings which are co-planar with respect to one another and orthogonal to the central benzene ring. Chemical-shift inequivalences are seen in the ^{13}C CPMAS NMR spectrum which can be attributed to the orientation of the phenyl rings with respect to the ether oxygen non-bonding orbitals. Qualitatively, the magnitudes of the chemical shift differences can be understood by an electric-field model for the neighbouring-group effect of the ether group. This allows the chemical shift-inequivalences observed in poly(aryl ether) compounds such as PEK (polyether ketone) to be related to the phenylene ring torsion angles. Variable-temperature NMR experiments demonstrate that the terminal phenyl rings execute π flips with an activation energy of 59.1 kJ mol^{-1} but that the central benzene ring must be flipping significantly slower. From the room-temperature crystal structure, torsional oscillations could be ruled out by the normal thermal parameters for the off-axis carbons. Owing to the disparity in the ring flipping rates, concerted π 'flips' can be eliminated. Molecular modelling of the crystalline 1,4-diphenoxybenzene is in hand to explore the manner in which intermolecular interactions influence the activation energy barriers to ring flipping for the central and terminal rings.

References

1 J. Schaefer, E. O. Stejskal, R. A. McKay, and W. T. Dixon, *Macromolecules*, 1984, **17**, 1479.
2 H. W. Spiess, *Colloid Polym. Sci.*, 1983, **261**, 193.
3 A. L. Cholli, J. J. Dumais, A. K. Engel, and L. W. Jelinski, *Macromolecules*, 1984, **17**, 2399.
4 N. J. Clayden, A. Bunn, and A. B. Newton, *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.*, 1988, **29**, 8.
5 K. Wüthrich, 'NMR in Biological Research: Peptides and Proteins,' Elsevier, Amsterdam, 1976.
6 I. D. Campbell, C. M. Dobson, G. R. Moore, S. J. Perkins, and R. J. P. Williams, *FEBS Lett.*, 1976, **70**, 96.
7 F. Inagaki, N. J. Clayden, N. Tamiya, and R. J. P. Williams, *Eur. J. Biochem.*, 1981, **120**, 313.
8 M. O'Connor, *Ciba Found. Symp.*, 1983, **93**.
9 A. N. Garroway, W. M. Ritchey, and W. B. Moniz, *Macromolecules*, 1982, **15**, 1051.
10 J. Schaefer, E. O. Stejskal, and R. Buchdahl, *Macromolecules*, 1977, **10**, 384.
11 M. Wehrle, G. P. Hellmann, and H. W. Spiess, *Colloid Polym. Sci.*, 1987, **265**, 815.
12 D. Perchak, J. Skolnick, and R. Yaris, *Macromolecules*, 1987, **20**, 121.
13 J. M. Twyman and C. M. Dobson, *J. Chem. Soc. Chem. Commun.*, 1988, 786.
14 P. M. Henrichs and H. R. Luss, *Macromolecules*, 1988, **21**, 860.
15 'High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk,' Methods in Stereochemical Analysis, vol 7, ed. R. A. Komoroski, VCH Publishers, Florida, USA, 1986.
16 J. Herzfeld and A. E. Berger, *J. Chem. Phys.*, 1980, **73**, 6021.
17 N. J. Clayden, C. M. Dobson, L.-Y. Lian, and D. J. Smith, *J. Magn. Reson.*, 1986, **69**, 476.
18 J. Jeneer, B. H. Meier, P. Bachmann, and R. R. Ernst, *J. Chem. Phys.*, 1979, **71**, 4546.
19 C. Connor, A. Naito, K. Takegoshi, and C. A. McDowell, *Chem. Phys. Lett.*, 1985, **113**, 123.
20 B. C. Laskowski, R. L. Jaffe, and A. Komornicki, *Int. J. Quantum Chem.*, 1986, **29**, 563.
21 F. Laupretre and L. Monnerie, *Eur. Polym. J.*, 1974, **10**, 21.
22 W. J. Horsley and H. Sternlicht, *J. Am. Chem. Soc.*, 1968, **90**, 3738.
23 N. J. Clayden, *Mag. Reson. Chem.*, 1989, **27**, 692.
24 (*a*) D. M. Rice, R. J. Wittebort, R. G. Griffin, E. Meirovitch, E. R. Stimson, Y. C. Meinwald, J. H. Freed, and H. A. Scheraga, *J. Am. Chem. Soc.*, 1981, **103**, 7707; (*b*) R. A. Kinsey, A. Kintanar, and E. Oldfield, *J. Biol. Chem.*, 1981, **256**, 9028; (*c*) D. M. Rice, Y. C. Meinwald, H. A. Scheraga, and R. G. Griffin, *J. Am. Chem. Soc.*, 1987, **109**, 1636.
25 J. M. Twyman, Personal communication.
26 D. Suwelack, W. P. Rothwell, and J. S. Waugh, *J. Chem. Phys.*, 1980, **73**, 2559.
27 W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Vetterling 'Numerical Recipes, The Art of Scientific Computing,' CUP, Cambridge, 1986, p. 498.
28 P. M. Henrichs, H. R. Luss, and R. P. Scaringe, *Macromolecules*, 1989, **22**, 2731.

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