The Structure of Poly(*m*-Phenylene): a Prediction from Single-crystal X-Ray Studies of *m*-Deciphenyl and *m*-Undeciphenyl

David J. Williams,*[a] Howard M. Colquhoun*[b] and Caroline A. O'Mahoney[a]

[a] *Department of Chemistry, Imperial College, London, UK SW7 2AY*
[b] *Imperial Chemical Industries plc, The Heath, Runcorn, UK WA7 4QE*

Single-crystal X-ray diffraction studies of the oligomers *m*-deciphenyl and *m*-undeciphenyl, isolated chromatographically from low molecular mass poly(*m*-phenylene), reveal disordered but unequivocally helical chain-structures, from which the crystal and molecular structure of poly(*m*-phenylene) can be directly inferred.

In recent years poly(*p*-phenylene) has been intensively studied, not only as a high-performance material[1] but also, after doping, for its potential as an organic conductor.[2] In contrast, the isomeric poly(*m*-phenylene) has generated only sporadic interest and little is known of its structure, even though an X-ray powder-pattern published in 1978 showed the polymer to be crystalline.[3] Very recently however, a U-shaped conformation identified for *m*-quinquephenyl in the solid state led the authors of that study to speculate on possible helical conformations for higher *m*-phenylene oligomers.[4] Such oligomers, C_6H_5–(m-C_6H_4)$_n$–C_6H_5 (n = 7–14), were first isolated in 1936 by fractional crystallisation of the products from palladium-catalysed coupling of *m*-dibromobenzene,[5] but almost sixty years later the structures of these oligomers and indeed that of poly(*m*-phenylene) itself still remained unknown. As part of a continuing programme of single-crystal X-ray studies of aromatic oligomers aimed at the prediction and analysis of high-performance polymer structures,[6] we have now investigated the crystal structures of *m*-deciphenyl and *m*-undeciphenyl as potential models for poly(*m*-phenylene).

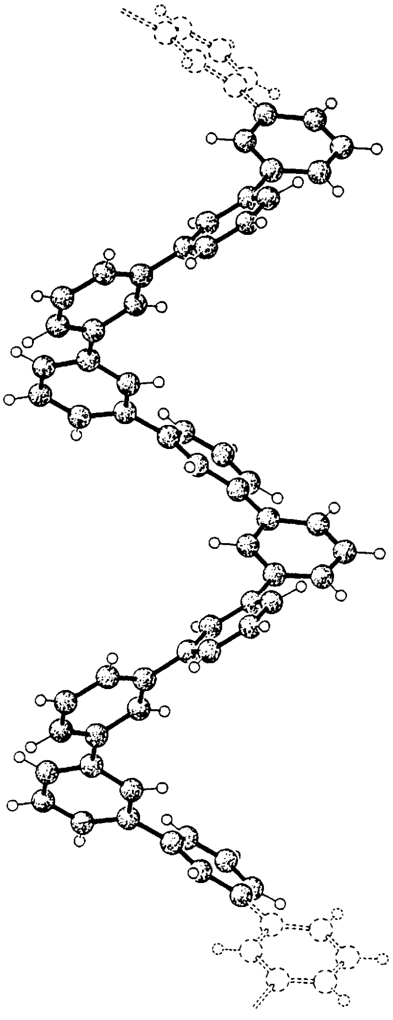

Fig. 1 The X-ray structure of *m*-deciphenyl, showing a single molecule within the pseudo-polymeric helical chain. The pitch of the helix is 11.22(1) Å, and independent arene–arene bond distances (Å) and associated mean inter-ring torsion angles (°) are: 1.49(1), 53(1); 1.50(1), 34(1); 1.47(1), 44(1).

Low molecular mass poly(*m*-phenylene)s were prepared from a mixture of *m*-dichlorobenzene (5 equiv.) and chlorobenzene (2 equiv.) using the homogeneous nickel-catalysed coupling reaction reported by Colon and Kelsey.[7] Milligram quantities of pure oligomers, C_6H_5–(m-C_6H_4)$_n$–C_6H_5 (n = 6–10), were isolated from this reaction by reverse-phase analytical HPLC with THF–water (6:4) as eluent. The identities of the oligomers were confirmed by mass spectrometry, the spectrum in each case showing a strong parent ion (both singly and doubly charged) and very little evidence of fragmentation under electron impact. Multiple fractionations by HPLC eventually yielded some 30 mg each of pure *m*-deciphenyl and *m*-undeciphenyl, from which it proved possible to obtain very small single crystals of both oligomers by slow evaporation of solutions in dichloromethane–chlorobenzene.†

The X-ray structure of *m*-deciphenyl, C_6H_5–(m-C_6H_4)$_8$–C_6H_5, reveals an apparently infinite, helical chain (Fig. 1), with five aromatic rings to each turn of the helix. Individual chains have crystallographic C_2 symmetry normal to the chain axis, are all of the same helicity as required by the polar tetragonal space group ($P4_12_12$ or $P4_32_12$), and are oriented with their long axes parallel to the crystallographic *c*-direction.

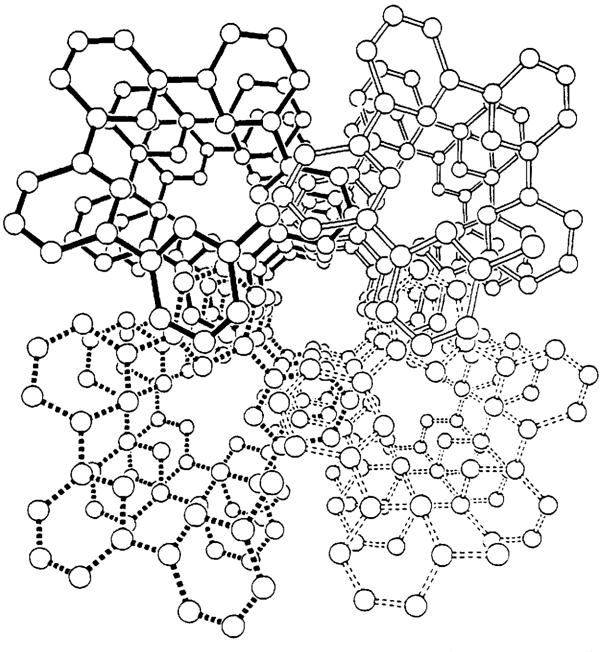

Fig. 2 Tetragonally packed, interleaving helical chains in the crystal of *m*-deciphenyl, viewed in perspective down the crystallographic *c*-direction

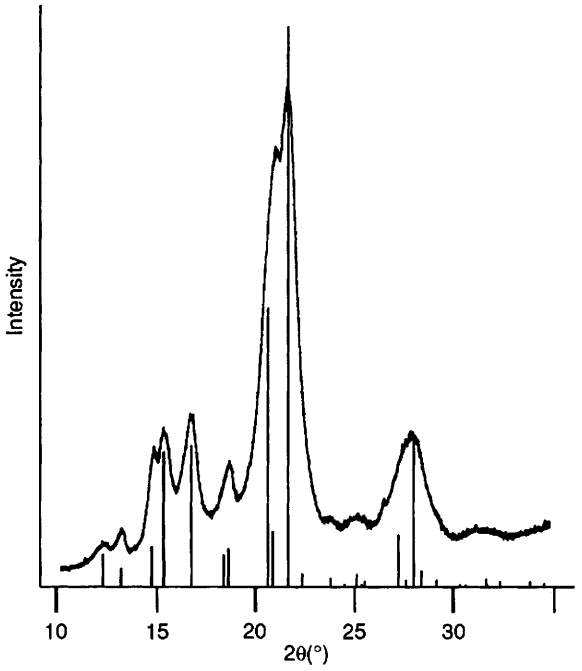

Fig. 3 X-Ray powder pattern (line diagram) calculated from the crystal structure of *m*-deciphenyl, superimposed on the experimental pattern (Cu-Kα) for poly(*m*-phenylene)

The unit cell contains eight asymmetric units, each comprising 2.5 aromatic rings. Adjacent helices interleave and pack in a tetragonal array, as shown in Fig. 2. Direct arene–arene bonds are normal at 1.48 ± 0.02 Å, and there are three independent inter-ring torsion angles repeating in the sequence 53, 34, 44, 44, 34°... along the chain. These angles may be compared with the values of 36, 31, −32, and 36° found in *m*-quinquephenyl which, because of its torsional sign-reversal, does not achieve a helical conformation.[4]

Although the crystal structure of *m*-deciphenyl is perhaps not obviously compatible with that of a monodisperse ten-ring oligomer, it can be shown to arise from longitudinal disorder associated with the presence of orthogonally arranged twofold axes normal to the chain direction. This form of crystallographic disorder results in a structure with well-defined (though partial-mass) atomic positions since, with the exception of hydrogen atoms at the oligomer chain-ends, individual atoms are either superposed by symmetry or are absent.‡ The existence of a polymer lattice with dominant generalised disorder is consistent with our observation that the eleven-ring oligomer, *m*-undeciphenyl, crystallises in the same space group as its ten-ring homologue, with identical (to within 3σ) unit cell dimensions. Below a certain chain-length however the concentration of chain-ends must be high enough to destabilise the polymer-type lattice since *m*-quinquephenyl does not adopt this structure.[4]

It has not escaped our notice that the structure we have identified immediately suggests a possible structure for poly(*m*-phenylene) itself. We have compared the X-ray powder pattern predicted from the structure of *m*-deciphenyl with an experimental pattern obtained for a sample of poly(*m*-phenylene) prepared by nickel-catalysed coupling of pure *m*-dichlorobenzene.[8]

The experimental pattern closely resembles, though is rather better-resolved than, a previously published powder pattern for poly(*m*-phenylene).[3] As shown in Fig. 3, the agreement in peak positions and relative intensities between the calculated and experimental data is very striking. This result provides strong evidence that, in the crystalline state, poly(*m*-phenylene) does indeed adopt the helical conformation and tetragonal chain-packing found in the oligomer structures reported here.

This work was supported by the Wolfson Foundation, and by a CASE award from the SERC and ICI plc. We wish to thank Dr M. E. B. Jones for encouragement, Dr A. C. Kemball for molecular graphics studies, and Dr S. J. Andrews for preliminary X-ray measurements.

Received, 9th May 1994; Com. 4/02736A

Footnotes

† *Crystal data*: $[C_{15}H_{10}]_n$, M = 190.2, tetragonal, a = 13.449(3), c = 11.216(6) Å, V = 2028.7(17) Å^3, space group $P4_12_12$ or enantiomorphous $P4_32_12$, Z = 8, D_c = 1.246 g cm^{-3}, μ(Cu-Kα) = 0.534 mm^{-1}, λ = 1.54178 Å, $F(000)$ = 800. Data for a crystal of dimensions 0.031 × 0.094 × 0.094 mm were measured on a Siemens P4RA diffractometer with Cu-Kα radiation (graphite monochromator) using ω-scans. Of the 1507 independent reflections measured, 638 had $|F_o| > 4\sigma(|F_o|)$ and were considered to be observed. The structure was solved by direct methods and the non-hydrogen atoms were refined anisotropically to give R = 0.073, R_w = 0.064. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ An alternative explanation for the apparently continuous molecular structure is that we have only identified a sub-lattice of the actual structure, and that there exists a superlattice with a unit cell having a *c*-axis length, which is an integer multiple of the value we have determined. However, searches for weak diffraction points associated with unit cells of this type have so far failed to reveal any measurable intensity.

References

1 P. Kovacic and M. B. Jones, *Chem. Rev.*, 1987, **87**, 357.
2 R. L. Elsenbaumer and L. W. Shacklette, *Handbook of Conducting Polymers*, ed. T. A. Skotheim, Marcel Dekker, New York, 1986, vol. 1, p. 213.
3 T. Yamamoto, Y. Hayashi and A. Yamamoto, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 2091.
4 P. W. Rabideau, A. Sygula, R. K. Dhar and F. R. Fronczek, *J. Chem. Soc., Chem. Commun.*, 1993, 1759.
5 M. Busch, W. Weber, C. Darboven, W. Renner, H. J. Hahn, G. Mathauser, F. Strätz, K. Zitzbaum and H. Englehardt, *J. Prakt. Chem.*, 1936, **146**, 1.
6 H. M. Colquhoun, C. A. O'Mahoney and D. J. Williams, *Polymer*, 1993, **34**, 218; H. M. Colquhoun, C. C. Dudman, D. J. Blundell, A. Bunn, P. D. Mackenzie, P. T. McGrail, E. Nield, J. B. Rose and D. J. Williams, *Macromolecules*, 1993, **26**, 107; C. A. O'Mahoney, D. J. Williams, H. M. Colquhoun, R. Mayo, S. M. Young, A. Askari, J. Kendrick and E. Robson, *Macromolecules*, 1991, **24**, 7527.
7 I. Colon and A. Kelsey, *J. Org. Chem.*, 1986, **51**, 2627.
8 M. Ueda, Y. Seino and J. Sugiyama, *Polym. J.*, 1993, **25**, 1319.