Neutron powder and \textit{ab initio} structure of ortho-xylene: the influence of crystal packing on phenyl ring geometry at 2 K†

Richard M. Ibberson,a* Carole Morrisonb and Michael Pragerc

\textit{a} ISIS Facility, CCLRC-Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, UK OX11 0QX.
E-mail: rmi@sisar.rl.ac.uk
\textit{b} Department of Chemistry, The University of Edinburgh, King’s Buildings, West Mains Road, Edinburgh, UK EH9 3JJ
\textit{c} Institut für Festkörperforschung, Forschungszentrum Jülich, 52425 Jülich, Germany

Received (in Oxford, UK) 27th October 1999, Accepted 24th February 2000
Published on the Web 15th March 2000

Crystal packing effects in the previously unknown structure of ortho-xylene are found to induce a high degree of strain to the phenyl ring which is not observed in high-level \textit{ab initio} structure calculations or in the crystal structures of the para and meta isomers; the potential for aromatic hydrogen bonding in the structure is discussed.

One motive for performing crystallographic studies on simple model systems is to reveal structural motifs that may be applicable to whole classes of compound. The wealth and understanding of these crystallographic data has led to the development of crystal engineering\textsuperscript{1} which is of increasing interest to organic and physical chemists. In addition such studies can be used in the derivation and testing of model systems.\textsuperscript{2,3} The wealth and understanding of these crystallographic data has led to the development of crystal engineering\textsuperscript{1} which is of increasing interest to organic and physical chemists. In addition such studies can be used in the derivation and testing of model systems.

Calculations for o-xylene (Fig. 1), assuming overall ideal \textit{C}_{2v} symmetry, show a significantly reduced distortion to the ring. In particular the C(1)–C(2) bond length is calculated at 1.412 Å—a discrepancy of 0.22 Å (> 7 standard deviations) as compared with the refined solid-state structure. Note, calculations were also made without the \textit{C}_{2v} symmetry constraint and starting from the crystal structure coordinates, but the same minimum was obtained. Subsequent refinement of a model assuming \textit{C}_{2v} symmetry against the neutron powder data, although resulting in a degraded fit to the pattern, was found to retain this discrepancy between the minimum-energy and solid-state conformation. Crystal packing effects in the structure of o-xylene thus appear to play a significant role in defining the molecular conformation.

In contrast, the calculated and experimentally determined solid-state conformations of the remaining isomers show excellent agreement. For \textit{m}-xylene the discrepancies in bond lengths determined in each case were typically 0.004 Å (1 standard deviation) with a maximum discrepancy for one phenyl-ring bond of 0.007 Å. For p-xylene the discrepancies in

![Fig. 1](image)

Fig. 1 (a) ORTEP\textsuperscript{17} diagram of the molecular conformation of \textit{o}-xylene at 2 K; thermal ellipsoids are drawn at the 50% probability level. Bond length (Å) and bond angle (°) values are shown with estimated standard deviations in parentheses determined from the neutron powder diffraction data. (b) Bond length (Å) and bond angle (°) values calculated \textit{ab initio} using the \textit{MP2}/6-31G* basis set. (Average values for bond lengths and bond angles around the methyl groups are: for C(1m) 1.093(3) Å, 110.85(3); for C(2m) 1.075(3) Å, 111.86(3) and from \textit{ab initio} calculation 1.095 Å, 111.27°.)

† Electronic supplementary information (ESI) available: neutron diffraction data and comparison of bond parameters from neutron and \textit{ab initio} data. See http://www.rsc.org/suppdata/chemcom/99/08599h/

\textsuperscript{5} Calculations for \textit{o}-xylene, assuming overall ideal \textit{C}_{2v} symmetry, show a significantly reduced distortion to the ring. In particular the C(1)–C(2) bond length is calculated at 1.412 Å—a discrepancy of 0.22 Å (> 7 standard deviations) as compared with the refined solid-state structure. Note, calculations were also made without the \textit{C}_{2v} symmetry constraint and starting from the crystal structure coordinates, but the same minimum was obtained. Subsequent refinement of a model assuming \textit{C}_{2v} symmetry against the neutron powder data, although resulting in a degraded fit to the pattern, was found to retain this discrepancy between the minimum-energy and solid-state conformation. Crystal packing effects in the structure of \textit{o}-xylene thus appear to play a significant role in defining the molecular conformation.

In contrast, the calculated and experimentally determined solid-state conformations of the remaining isomers show excellent agreement. For \textit{m}-xylene the discrepancies in bond lengths determined in each case were typically 0.004 Å (1 standard deviation) with a maximum discrepancy for one phenyl-ring bond of 0.007 Å. For \textit{p}-xylene the discrepancies in

\textsuperscript{5} Calculations for \textit{o}-xylene, assuming overall ideal \textit{C}_{2v} symmetry, show a significantly reduced distortion to the ring. In particular the C(1)–C(2) bond length is calculated at 1.412 Å—a discrepancy of 0.22 Å (> 7 standard deviations) as compared with the refined solid-state structure. Note, calculations were also made without the \textit{C}_{2v} symmetry constraint and starting from the crystal structure coordinates, but the same minimum was obtained. Subsequent refinement of a model assuming \textit{C}_{2v} symmetry against the neutron powder data, although resulting in a degraded fit to the pattern, was found to retain this discrepancy between the minimum-energy and solid-state conformation. Crystal packing effects in the structure of \textit{o}-xylene thus appear to play a significant role in defining the molecular conformation.

In contrast, the calculated and experimentally determined solid-state conformations of the remaining isomers show excellent agreement. For \textit{m}-xylene the discrepancies in bond lengths determined in each case were typically 0.004 Å (1 standard deviation) with a maximum discrepancy for one phenyl-ring bond of 0.007 Å. For \textit{p}-xylene the discrepancies in

\textsuperscript{5} Calculations for \textit{o}-xylene, assuming overall ideal \textit{C}_{2v} symmetry, show a significantly reduced distortion to the ring. In particular the C(1)–C(2) bond length is calculated at 1.412 Å—a discrepancy of 0.22 Å (> 7 standard deviations) as compared with the refined solid-state structure. Note, calculations were also made without the \textit{C}_{2v} symmetry constraint and starting from the crystal structure coordinates, but the same minimum was obtained. Subsequent refinement of a model assuming \textit{C}_{2v} symmetry against the neutron powder data, although resulting in a degraded fit to the pattern, was found to retain this discrepancy between the minimum-energy and solid-state conformation. Crystal packing effects in the structure of \textit{o}-xylene thus appear to play a significant role in defining the molecular conformation.

In contrast, the calculated and experimentally determined solid-state conformations of the remaining isomers show excellent agreement. For \textit{m}-xylene the discrepancies in bond lengths determined in each case were typically 0.004 Å (1 standard deviation) with a maximum discrepancy for one phenyl-ring bond of 0.007 Å. For \textit{p}-xylene the discrepancies in

\textsuperscript{5} Calculations for \textit{o}-xylene, assuming overall ideal \textit{C}_{2v} symmetry, show a significantly reduced distortion to the ring. In particular the C(1)–C(2) bond length is calculated at 1.412 Å—a discrepancy of 0.22 Å (> 7 standard deviations) as compared with the refined solid-state structure. Note, calculations were also made without the \textit{C}_{2v} symmetry constraint and starting from the crystal structure coordinates, but the same minimum was obtained. Subsequent refinement of a model assuming \textit{C}_{2v} symmetry against the neutron powder data, although resulting in a degraded fit to the pattern, was found to retain this discrepancy between the minimum-energy and solid-state conformation. Crystal packing effects in the structure of \textit{o}-xylene thus appear to play a significant role in defining the molecular conformation.

In contrast, the calculated and experimentally determined solid-state conformations of the remaining isomers show excellent agreement. For \textit{m}-xylene the discrepancies in bond lengths determined in each case were typically 0.004 Å (1 standard deviation) with a maximum discrepancy for one phenyl-ring bond of 0.007 Å. For \textit{p}-xylene the discrepancies in
bond lengths determined in each case were typically 0.008 Å (2 standard deviations) with a maximum discrepancy for one phenyl-ring bond of 0.012 Å. The most significant differences in each case were observed for the torsions of the methyl groups. Rotations of 6 and 23° compared to the minimum-energy conformation are observed for m-xylene, and 6° (one clockwise, one anticlockwise) for p-xylene. However, as the vibrational frequencies calculated (b3pw91/6-31G*) for these low energy torsional modes are only 21 and 24 cm⁻¹, respectively, it is not surprising that crystal packing forces have distorted the ring substituents from their idealised torsional values.

The o-xylene crystal structure has, on inspection of the intermolecular contacts (Fig. 2), the potential for ‘aromatic hydrogen bonding’ (see for example ref. 12). The closest contact from the midpoint of the phenyl ring to a methyl, D(21), atom of a neighbouring molecule is 2.816(4) Å. The distances of this D(21) atom to the six individual C atoms lie in a broad range of 2.849–3.422 Å. The two shortest contacts with the C(1) and C(2) atoms are 2.849(4) and 2.908(5) Å, respectively, which is significantly less that the sum of the van der Waals radii at 3.05 Å for C(2) atoms are 2.849(4) and 2.908(5) Å.

It is now generally recognised that C•H groups can act as weak hydrogen bond donors 13 and there is a growing literature on the subject particularly in the context of crystal engineering cited earlier. The documentation and characterisation of these weak interactions is well advanced only in the case for bonds formed between C•H donors and oxygen acceptors. The interactions between other weak donor–acceptor combinations, especially as in the present case of such a weakly polarized donor group as Me with a π-acceptor, is considerably less well characterized. Nevertheless, electron donation from a Me group of a neighbouring molecule into an antibonding aromatic orbital seems the most plausible explanation for the unusual lengthening of the disubstituted C=C bond in the solid-state structure of o-xylene.

We thank Dr C. C. Wilson for helpful discussions during the course of this work. Acknowledgement is made to the EPSRC for the provision of beam time at the ISIS Facility and for the Edinburgh ab initio facilities (grant GR/K/04194).

Notes and references

1. Data were recorded using a vanadium-tailed helium-flow ‘orange’ crystal over a time-of-flight range of 30–230 ms corresponding to a d-spacing range of 0.6–4 Å at backscattering (× 2.0 = 168°). Lower angle (90 and 30°) detector banks enabled d-spacings of, in this case, up to 6.0 Å to be recorded, albeit at lower resolution, for the purposes of unit cell indexing.

2. Crystal data for ortho-xylene: C₉D₈O, M = 116.23, monoclinic, space group P2₁/a (no. 14), a = 12.3114(1), b = 6.0714(1), c = 8.8157(1), β = 108.884(1)°, U = 634.36(1) Å³, T = 2 K, Z = 4. The unit cell was determined automatically from 36 low-order reflections 2.4 < d < 6.0 Å using program ITO. The structure was solved by direct methods (MITHRIL) and refined without the use of bond length or bond angle constraints using the Rietveld method implemented by program TF12LS. 10

3. Only the D atoms were refined anisotropically. R₁ = 1.62%, R₂ = 3.38%, R₃ = 3.90%, χ² = 3.63 for 6579 observations and 145 basic variables.

4. All ab initio calculations were performed on a DEC Alpha AFX 1000 workstation using the GAUSSIAN 94 program. 18 A graded series of calculations were undertaken for all three compounds using the standard gradient techniques at the SCF and b3pw91 levels of theory using the 6-31G* basis set. Vibrational frequencies calculated from analytic second derivatives at the b3pw91/6-31G* level confirmed the Cᵥ symmetry grouping for o-xylene, C for m-xylene and G for p-xylene as minimum on their respective potential energy surfaces. Further calculations were then undertaken for o-xylene firstly, to confirm the Cᵥ structure as the global minimum an optimisation was performed (b3pw91/6-31G*) starting from the crystal structure coordinates with no symmetry constraints. From an observation of the absolute energies obtained it was clear that removal of the symmetry constraints resulted in exactly the same minima being obtained in the optimisation. Finally the potential energy surfaces were re-optimised with the crystal structure parameters one further higher level calculation (MP2/6-31G*) was undertaken. At this level all geometric parameters were observed to be effectively converged within the series of calculations performed, with e.g. C=C bond distances varying by < 0.3 pm and all angles by < 0.2° for improvements in basis set at the MP2 level. It can therefore be concluded that any further higher level calculations are unlikely to result in significant changes in molecular geometry.

8. C. J. Gilmore, MITHRIL a computer program for the automatic solution of crystal structures from X-ray data (Version 1.0), Department of Chemistry, University of Glasgow, Glasgow, UK GI2 8QG, 1983.

Fig. 2 Geometry of the aromatic ring–methyl group interactions. (Primed atoms denote symmetry code i=x, -iy, z; m denotes the midpoint of the phenyl ring.)

Communication a005399h