

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

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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 *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 engineering¹ which is of increasing interest to organic and physical chemists. In addition such studies can be used in the derivation and testing of model potentials^{2,3} which is the background to the present study. Though the three isomers of xylene are familiar laboratory compounds, until recently little was known about their structure in the solid state.^{2,4,5} We now describe the crystal structure of *o*-xylene at low temperature which, in contrast to the other isomers, exhibits a strained ring conformation which we suggest may be attributed to weak intermolecular forces.

A 2 g powder sample of perdeuterated *o*-xylene was prepared by the method described in ref. 6 and neutron powder diffraction data‡ were collected at 2 K on the High Resolution Powder Diffractometer, HRPD, at the ISIS pulsed-neutron source, UK. The structure was solved§ routinely from the powder data using direct methods to reveal a monoclinic phase of cell volume 634 Å³; space group *P2*₁/*a*. The four molecules in the unit cell are arranged in columns running along the unit cell *a* axis in a herring-bone configuration with D⋯D contact distances of ca. 2.4–2.8 Å.

Examination of the refined molecular conformation (Fig. 1) reveals the determination of bond lengths and bond angles to be both precise and accurate as is expected from a high-resolution study on a structure of this limited complexity. The conformation shows small but significant deviations from *C*_{2v} symmetry, but most striking is the deformation of the carbon skeleton of the phenyl ring between the two substituted carbon atoms C(1) and C(2). The observed bond length of 1.433(3) Å is considerably in excess of the distance expected on consideration of steric repulsion of the eclipsed methyl groups and possible conjugation effects due to the substituent methyl groups. This finding is in contrast to the minor ring deformation observed in the crystal structures of the *meta* and *para* isomers⁵ determined from neutron powder diffraction data and, for example, the negligible deformation seen in the X-ray single crystal study of *ortho*-dinitrobenzene,¹¹ all of which are found to be in accord with expected conjugation effects. Accordingly, a series of high-level *ab initio* calculations¶ were undertaken in order to establish the minimum energy conformation of the *ortho*, *meta* and *para* isomers.

† Electronic supplementary information (ESI) available: neutron diffraction data and comparison of bond parameters from neutron and *ab initio* data. See <http://www.rsc.org/suppdata/cc/a9/a908599h/>

Calculations for *o*-xylene (Fig. 1), assuming overall ideal *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 *C*_{2v} symmetry constraint and starting from the crystal structure coordinates, but the same minimum was obtained. Subsequent refinement of a model assuming *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 *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

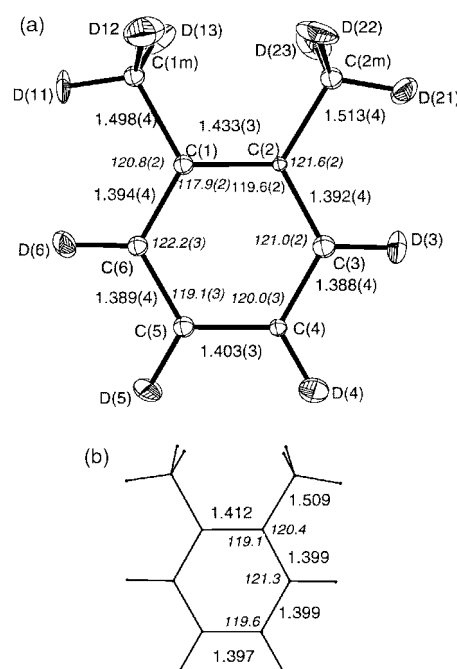


Fig. 1 (a) ORTEP¹⁷ diagram of the molecular conformation of *o*-xylene at 2 K; thermal ellipsoids are drawn at the 50% probability level. Bond length (Å) and bond angle (°) values are shown with estimated standard deviations in parentheses determined from the neutron powder diffraction data. (b) Bond length (Å) and bond angle (°) values calculated *ab initio* using the MP2/6-311G* 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 *ab initio* calculation 1.095 Å, 111.27°.)

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 than the sum of the van der Waals radii at 3.05 Å, and, most notably the distance from the C(1)–C(2) bond midpoint to D(21) is only 2.789(4) Å, making an angle of 152.6(3)° with the methyl group C–D bond. No other significant contacts are made to C(1) and C(2), in contrast with the remaining four phenyl C atoms which typically have three or more contacts in the range 2.86–3.1 Å. The contact is made off-centre to the phenyl ring and in general would be regarded as less favourable for an interaction, however, in this case it is the apparent directional (as opposed to isotropic) nature of the contact which correlates well with the observed molecular conformation. It is this strong directional nature of the contact that leads us to suppose it to be a significant interaction.

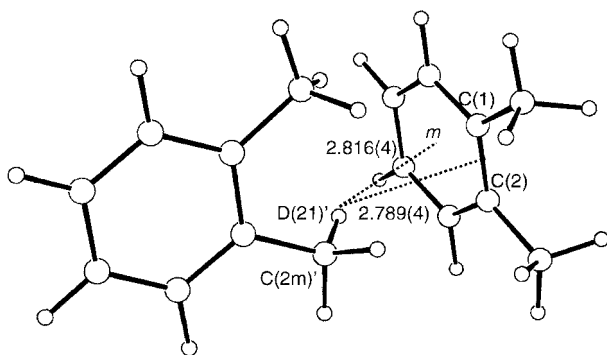


Fig. 2 Geometry of the aromatic ring–methyl group interactions. (Primed atoms denote symmetry code $\frac{1}{2}-x, -\frac{1}{2}+y, -z$; *m* denotes the midpoint of the phenyl ring.)

It is now generally recognised that C–H groups can act as weak hydrogen bond donors^{13–16} and there is a growing literature on the subject particularly in the context of crystal engineering cited earlier. The documentation and characterization 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.

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Notes and references

‡ Data were recorded using a vanadium-tailed helium-flow 'orange' cryostat over a time-of-flight range of 30–230 ms corresponding to a *d*-spacing range of 0.6–4.6 Å at backscattering ($\langle 2\theta \rangle = 168^\circ$). 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.

§ Crystal data for *ortho*-xylene: C₈D₁₀, *M* = 116.23, monoclinic, space group *P*2₁/*a* (no.14), *a* = 12.5114(1), *b* = 6.0714(1), *c* = 8.8157(1) Å, β = 108.6847(4)°, *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.⁷ The structure was solved by direct methods (MITHRIL)⁸ and refined without the use of bond length or bond angle constraints using the Rietveld method⁹ implemented by program TF12LS.¹⁰ Only the D atoms were refined anisotropically. *R*_c = 1.62%, *R*_p = 3.38%, *R*_{wp} = 3.90%, χ^2 = 3.63 for 6579 observations and 145 basic variables.

¶ All *ab initio* calculations were performed on a DEC Alpha APX 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 C_{2v} symmetry grouping for *o*-xylene, C_s for *m*-xylene and C_i for *p*-xylene as minimum on their respective potential energy surfaces. Further calculations were then undertaken for *o*-xylene: firstly, to confirm the C_{2v} 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, for direct comparison with the crystal structure parameters one further higher level calculation (MP2/6-311G*) 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.

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