



THE UNIVERSITY *of* EDINBURGH

Edinburgh Research Explorer

Predicting anisotropic displacement parameters using molecular dynamics

Citation for published version:

Morrison, C, Reilly, AM, Wann, D, Gutmann, MJ, Jura, M & Rankin, D 2013, 'Predicting anisotropic displacement parameters using molecular dynamics: density functional theory plus dispersion modelling of thermal motion in benzophenone' *Journal of Applied Crystallography*, vol 46, no. Part 3, pp. 656-662. DOI: 10.1107/S0021889813006225

Digital Object Identifier (DOI):

[10.1107/S0021889813006225](https://doi.org/10.1107/S0021889813006225)

Link:

[Link to publication record in Edinburgh Research Explorer](#)

Document Version:

Publisher's PDF, also known as Version of record

Published In:

Journal of Applied Crystallography

Publisher Rights Statement:

Copyright © 2013 International Union of Crystallography. All rights reserved.

General rights

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact openaccess@ed.ac.uk providing details, and we will remove access to the work immediately and investigate your claim.



Predicting anisotropic displacement parameters using molecular dynamics: density functional theory plus dispersion modelling of thermal motion in benzophenone

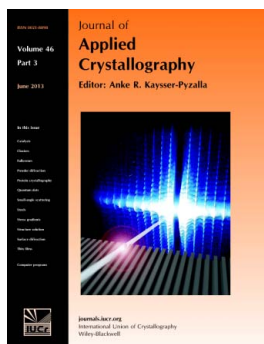
Anthony M. Reilly, Derek A. Wann, Matthias J. Gutmann, Marek Jura, Carole A. Morrison and David W. H. Rankin

J. Appl. Cryst. (2013). **46**, 656–662

Copyright © International Union of Crystallography

Author(s) of this paper may load this reprint on their own web site or institutional repository provided that this cover page is retained. Reproduction of this article or its storage in electronic databases other than as specified above is not permitted without prior permission in writing from the IUCr.

For further information see <http://journals.iucr.org/services/authorrights.html>



Journal of Applied Crystallography covers a wide range of crystallographic topics from the viewpoints of both techniques and theory. The journal presents papers on the application of crystallographic techniques and on the related apparatus and computer software. For many years, the *Journal of Applied Crystallography* has been the main vehicle for the publication of small-angle scattering papers and powder diffraction techniques. The journal is the primary place where crystallographic computer program information is published.

Crystallography Journals **Online** is available from journals.iucr.org

Predicting anisotropic displacement parameters using molecular dynamics: density functional theory plus dispersion modelling of thermal motion in benzophenone

Anthony M. Reilly,^{a*‡} Derek A. Wann,^{a*} Matthias J. Gutmann,^b Marek Jura,^b Carole A. Morrison^a and David W. H. Rankin^a

^aEaStCHEM School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ, Scotland, and ^bISIS Facility, Rutherford Appleton Laboratory-STFC, Chilton, Didcot, Oxfordshire OX11 0QX, England. Correspondence e-mail: reilly@fhi-berlin.mpg.de, derek.wann@ed.ac.uk

The benefits of combining experimental and computational methods have been demonstrated by a study of the dynamics and solid-state structure of α -benzophenone. Dispersion-corrected and -uncorrected density functional theory molecular dynamics simulations were used to obtain displacement parameters, with the dispersion-corrected simulations showing good agreement with the experimental neutron and X-ray diffraction values. At 70 K, quantum-nuclear effects resulted in poor values for the hydrogen atoms, but the heavy-atom values still show excellent agreement, suggesting that molecular dynamics simulations can be a useful tool for determining displacement parameters where experimental data are poor or limited.

© 2013 International Union of Crystallography
Printed in Singapore – all rights reserved

1. Introduction

In the past 20 years there have been many advances in the tools and techniques used to study condensed-phase systems. The continued development of neutron sources and synchrotron X-ray facilities, in tandem with the phenomenal growth in the application of density functional theory (DFT), has greatly improved our understanding of the structure and function of numerous materials and systems. However, there remain many challenges at the frontiers of crystallography, which in turn hinder our ability to study and understand new and complex materials. Studies at high pressure and temperature or of macromolecular systems often have a limited range of data, which greatly complicates the refinement process. The modelling of thermal motion *via* the Debye–Waller factor is important to the quality of a fit but it also increases the number of parameters to be fitted and thus requires more data. The refinement of displacement parameters for light atoms in single-crystal X-ray diffraction experiments, where more than enough data can easily be collected, can also be difficult because of the lack of scattering from these atoms.

Theoretical methods offer a way of supplementing the information obtained from diffraction experiments. It is common in gas electron diffraction studies to use theoretically determined vibrational and structural information as restraints (Blake *et al.*, 1996; Brain *et al.*, 1996; Mitzel & Rankin, 2003) and corrections (McCaffrey *et al.*, 2007; Sipachev, 1985, 2001, 2000; Wann *et al.*, 2009) to counter the limited

nature of the data. Our recent work on vibrations in crystals has focused on using molecular dynamics (MD) simulations to probe the nature of anharmonic thermal motion, providing corrections that convert time-averaged experimental structures to equilibrium ones (Reilly *et al.*, 2007, 2010b), as well as model data sets for assessing new anharmonic Debye–Waller factors (Reilly, Morrison & Rankin, 2011; Reilly, Morrison, Rankin & McLean, 2011). However, MD simulations also offer a route to information on the harmonic parameters that define the standard anisotropic (displacement ellipsoid) model. The harmonic model used to describe thermal motion in many refinements requires six anisotropic displacement parameters (ADPs), U_{ij} , which are elements of the co-variance matrix, \mathbf{U} , of a three-dimensional probability density function (PDF) that describes an atom's thermal motion, P :

$$P(\mathbf{u})_{\text{harm}} = \frac{\det(\mathbf{U}^{-1/2})}{(2\pi)^{3/2}} \exp\left(-\frac{1}{2} \mathbf{u}^T \mathbf{U}^{-1} \mathbf{u}\right), \quad (1)$$

where \mathbf{u} is an atomic displacement and T denotes the transpose of the matrix. The co-variance matrix can be calculated numerically from an MD trajectory. Alternatively, a one-dimensional isotropic PDF can be used, based on a single variance parameter U_{eq} that describes the extent of thermal motion averaged over the three directions. Glykos (2007) has used empirical-potential MD simulations of a small protein crystal structure to calculate ADPs, which were of some use in parameterizing refinements.

A variety of methods have been devised to estimate light-atom ADPs from heavy-atom values. This is important for

[‡] Present address: Fritz-Haber-Institut der MPG, Faradayweg 4–6, D-14195 Berlin, Germany.

charge-density studies, where the convolution of the electron density and vibrational PDF means that meaningful interpretation of the refined electron-density maps requires a good description of thermal motion. The **TLS** method (Schomaker & Trueblood, 1968), which assumes motion of rigid molecules, can be used to extrapolate heavy-atom ADPs to H atoms by determining the librational (**L**) and translational (**T**) motion tensors of a molecule. More sophisticated schemes, including the **TLS+ONIOM** method (Whitten & Spackman, 2006), combine the rigid **TLS** model with *ab initio* computed estimates of the contribution from internal degrees of freedom. The *SHADE* web server can perform the requisite **TLS** analysis of an experimental refinement and provides empirical estimates of the contribution of non-rigid motions (Madsen, 2006).

For systems where there are no heavy-atom ADPs, prediction of displacement parameters can only be achieved readily using lattice dynamics (LD) or MD simulations. LD calculations (Dove, 2005; Baroni *et al.*, 2001) can be performed in a variety of ways but the method in essence uses a series of static calculations of a perturbed system to determine its normal-mode eigenvectors and eigenvalues. LD has been used a number of times to compute ADPs for a number of different types of systems (Criado *et al.*, 1984; Pilati *et al.*, 1998). One of the main benefits of LD is the direct inclusion of zero-point energy contributions and the ability to model phonon dispersion using calculations at different parts of the Brillouin zone, without having to resort to the use of supercells as in an MD simulation. However, the principal disadvantage of LD calculations is that they are nearly always performed in the harmonic limit. At high temperatures, attempting to fit an anharmonic potential with a harmonic one may lead to spurious results, as we have seen for an equivalent situation in the gas phase (Wann *et al.*, 2008, 2009).

As LD calculations are liable to be best suited to low-temperature nearly harmonic systems, MD simulations should be complementary, as they are best suited to high-temperature systems (for classical MD simulations, which omit quantum nuclear effects) and can deal with any degree of anharmonicity. In this present work, we explore the possibility of using MD to derive both ADPs and equilibrium corrections by studying the crystal structure of benzophenone using a combination of DFT–MD simulations and neutron diffraction data.

The solid-state structure of benzophenone ($C_{13}H_{10}O$) has been studied a number of times using X-ray diffraction, and two phases or polymorphs (one stable, one metastable) are known in the literature (Fleischer *et al.*, 1968; Moncol & Coppens, 2004; Kutzke *et al.*, 2000). Indeed, benzophenone was the first organic compound reported to exhibit polymorphism (Gossner, 1904). This present study focuses on the stable α phase, which crystallizes in the orthorhombic $P2_12_12_1$ space group. No neutron diffraction structure of either phase has been reported before now. Owing to its numerous π bonds, the solid-state interactions between benzophenone molecules will be dominated by dispersion forces, which standard DFT models quite poorly. Therefore, this study allows us to inves-

tigate how serious a deficiency this is for DFT simulations of ADPs and whether or not pairwise dispersion corrections (Grimme, 2004; Elstner *et al.*, 2001) to DFT can improve its modelling of thermal motion in organic crystals.

The following section outlines the experimental and computational approach. Thereafter is a discussion of the experimental refinements and comparison with the MD simulation results. Finally, we discuss the effect of the thermal motion on the structural parameters of the molecule.

2. Methods

2.1. Experimental

Single-crystal neutron diffraction data were collected on the SXD instrument at the ISIS spallation neutron source, Rutherford Appleton Laboratories, Oxfordshire, England (Keen *et al.*, 2006). The SXD instrument uses the time-of-flight Laue diffraction method and is capable of capturing large amounts of reciprocal space with a stationary crystal, making use of the large area of the detectors used in the instrument.

Undeuterated crystals of benzophenone were grown by cooling from 323 to 293 K over a period of 48 h. From this batch, a crystal of approximately $6 \times 7 \times 2$ mm was selected for use in the diffraction experiment. Data were collected at temperatures of 70 and 300 K. To maximize the number of observed reflections, eight crystal orientations were used at each temperature. The *SXD2001* program (Gutmann, 2005) was used to index the unit cells and to reduce the raw data to a format suitable for refinement. Refinements were carried out using the *SHELX97* program (Sheldrick, 2008), starting from coordinates from a previous X-ray structure of benzophenone (Moncol & Coppens, 2004). Extinction was modelled as part of the structure refinement using the *SHELX97* extinction model and the wavelength for each reflection.

To complement the high-temperature neutron diffraction data set, X-ray diffraction data were collected at 295 K using an Oxford Diffraction Gemini S diffractometer equipped with a Sapphire CCD detector using $Mo K\alpha$ radiation with a wavelength of 0.71073 Å. Refinement was also carried out using *SHELX97*, with the C- and O-atom positions being refined using anisotropic displacement parameters, while the H atoms were fixed and treated isotropically.

2.2. MD simulations

All of the DFT simulations of the crystal structure of benzophenone were carried out using the Gaussian and plane-wave formalism (Lippert *et al.*, 1997), as incorporated in the *CP2K* code (VandeVondele *et al.*, 2005). The generalized gradient-corrected PBE functional (Perdew *et al.*, 1996) was used, together with the PBE-optimized double- ζ basis set provided with the code. The analytical pseudopotentials of Goedecker and co-workers (Goedecker *et al.*, 1996; Hartwigsen *et al.*, 1998; Krack, 2005) were used, together with a plane-wave density cutoff energy of 4250 eV. This value ensured convergence of the atomic forces and the total energy to within 2 meV \AA^{-1} and 1 meV atom^{-1} , respectively. For

some simulations an empirical correction for van der Waals dispersion was added. The van der Waals-corrected DFT calculations will be referred to as DFT+D calculations. The correction used the functional form of Elstner *et al.* (2001), together with the PBE-optimized C_6 and R_0 parameters of Williams & Malhotra (2006). We note that there are more recent and potentially more suitable C_6 parameters available (Grimme *et al.*, 2010; Tkatchenko & Scheffler, 2009). However, different parameters are unlikely to affect the qualitative insights of applying the benzene-optimized parameters used here.

Equilibrium geometries were determined for both the DFT and DFT+D levels of theory. As the *CP2K* program does not currently support symmetry constraints, a $2 \times 2 \times 2$ supercell was optimized with $P1$ symmetry and the equilibrium geometry determined by averaging coordinates of the optimized geometry using the $P2_12_12_1$ set of symmetry operations. The deviations between the average symmetry-related positions were of the order of 1 fm, which is well within the error of an experimental structure.

MD simulations were performed using a $2 \times 2 \times 2$ supercell both with and without the van der Waals correction term. A chain of five Nosé–Hoover thermostats (Nosé, 1984; Hoover, 1985) was used to maintain the temperature. In total, three production simulations were performed. Initial problems with the experimental data collected as part of this study led to two simulations being performed at 300 K using the previously reported 90 K cell vectors of Moncol & Coppens (2004). The DFT simulation was run for 9 ps, while the DFT+D simulation was run for 14 ps. Finally, a 13 ps DFT+D simulation was performed at a temperature of 70 K using lattice constants of $a = 7.7307$, $b = 10.2535$ and $c = 12.0542$ Å. These values were obtained from a preliminary refinement of the 70 K neutron diffraction data set. Using the different lattice parameters at 70 and 300 K will give rise to minor deviations from atmospheric pressure in the MD simulations. We do not anticipate this effect to be significant for a molecular solid over the pressure range expected.

The trajectories were analysed numerically to determine the mean atomic position and ADPs using the method described

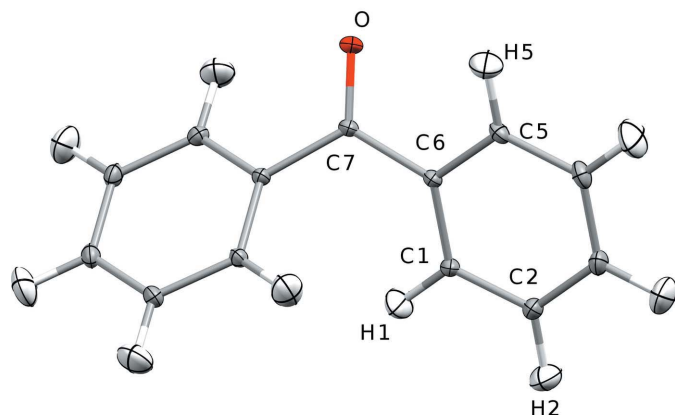


Figure 1
The 70 K experimental structure of benzophenone, with displacement ellipsoids plotted at the 50% probability level.

Table 1
Crystallographic data at 70, 295 and 300 K for benzophenone.

Parameter	70 K (neutron)	295 K (X-ray)	300 K (neutron)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	7.7145 (15)	7.996 (5)	7.979 (3)
b (Å)	10.2301 (18)	10.291 (5)	10.274 (3)
c (Å)	12.0269 (18)	12.174 (5)	12.103 (4)
V (Å ³)	949.2 (3)	1001.7 (3)	992.2 (5)
Total number of reflections	13371	1915	5557
Independent reflections/ parameters	13371/225	1915/128	5557/225
R factor [$R(F^2)$]	0.0914	0.0914	0.0904
Weighted R factor [$wR(F^2)$]	0.2068	0.0790	0.2243
Goodness of fit (S)	1.044	0.971	1.070
Maximum and minimum density differences (e Å ⁻³)	2.673, -1.594	0.104, -0.103	0.597, -0.789
w_{r1}	0.1421	0.0220	0.1923
w_{r2}	0.0000	0.0000	1.9468

previously (Reilly *et al.*, 2007, 2010*a,b*). The first few picoseconds of the trajectory were removed to allow for thermal equilibration of the simulation. The central limit theorem (Allen & Tildesley, 1989) and the blocking method (Flyvbjerg & Petersen, 1989) were used to estimate the sampling uncertainties of the quantities determined from the trajectory.

3. Results and discussion

3.1. Crystallographic structures and displacement parameters

3.1.1. Details of neutron and X-ray refinements. Anisotropic neutron diffraction refinements were carried out using the 70 and 300 K data sets, while a mixed anisotropic/isotropic refinement was performed on the 295 K X-ray diffraction data set, with the H-atom positions fixed relative to those of the C atoms. The crystallographic data and refinement parameters determined are given in Table 1.¹ A statistical weighting scheme of $w = 1/[\sigma^2(F_o^2) + (w_{r1}P)^2 + w_{r2}P]$, where $P = (F_o^2 + 2F_c^2)/3$, was used for all of the refinements discussed here. The parameters w_{r1} and w_{r2} are different for the three refinements and are reported in Table 1.

The refinements are satisfactory for all three sets of data, although we note that the R factor for the 70 K neutron data set is somewhat high for a low-temperature data set, but this likely stems from the time-of-flight nature of the diffraction apparatus, which can introduce additional sources of uncertainty and often gives larger R factors than fixed wavelength methods. The X-ray diffraction results, obtained using the same batch of crystals, show that the crystals are of suitable quality for diffraction.

3.1.2. Comparison of experimental structures. The molecular structure of benzophenone is shown in Fig. 1, together with the 70 K displacement ellipsoids. In Table 2 a comparison is made of selected bond lengths in the molecule obtained from the three different refinements. As the X-ray refinement

¹ Supplementary data for this paper are available from the IUCr electronic archives (Reference: KK5130). Services for accessing these data are described at the back of the journal.

Table 2

Selected bond distances and isotropic displacement parameters from the 70, 295 and 300 K crystallographic refinements.

Note that the constrained nature of the X-ray refinement prevents the determination of uncertainties for the H-atom displacement parameter. The atomic numbering is as defined in Fig. 1.

Bond lengths (Å)	70 K (neutron)	295 K (X-ray)	300 K (neutron)
C1–C2	1.390 (2)	1.382 (3)	1.384 (4)
C1–H1	1.083 (4)	0.96 (2)	1.091 (8)
C5–H5	1.080 (4)	0.96 (2)	1.078 (9)
C1–C6	1.401 (2)	1.387 (3)	1.386 (4)
C6–C7	1.493 (2)	1.489 (3)	1.484 (4)
C7–O	1.223 (2)	1.224 (3)	1.219 (4)

U_{eq} (Å ²)	70 K (neutron)	295 K (X-ray)	300 K (neutron)
C1	0.0097 (2)	0.0602 (6)	0.0549 (7)
H1	0.0246 (8)	0.076	0.083 (2)
C2	0.0118 (3)	0.0721 (7)	0.0687 (9)
H2	0.0295 (9)	0.087	0.107 (3)
C6	0.0084 (2)	0.0534 (5)	0.0516 (7)
C7	0.0087 (2)	0.0599 (6)	0.0563 (7)
O	0.0152 (4)	0.0952 (6)	0.0875 (14)

took no account of the nonspherical nature of the electronic distribution, the C–H bond lengths are nonphysical, with values of less than 1 Å, which is common in X-ray crystallography studies. The heavy-atom bond lengths agree reasonably between all three refinements, with the higher-temperature data set yielding mainly shorter bonds, as would be expected owing to librational thermal motion. However, the uncertainties mean that, in some cases, the bond lengths cannot be differentiated between the different refinements and temperatures.

While there are only small differences between the bond lengths at 70 and 300 K, the isotropic displacement parameters at 295 and 300 K are significantly larger than those at 70 K, being on average three to six times the size at the higher temperature. We do not expect the H-atom values to agree well between the X-ray and neutron diffraction data sets, but the good agreement of the C and O displacement parameters is a further indication of the quality and reliability of the neutron diffraction data.

3.2. Molecular dynamics simulations results

3.2.1. Displacement parameters. Table 3 gives some representative U_{eq} values calculated from the MD simulations at 70 and 300 K, together with the experimentally refined neutron diffraction values. At 300 K, all of the DFT and DFT+D U_{eq} values are smaller than the corresponding experimental values. However, the DFT+D values are significantly larger than the uncorrected DFT ones, the mean absolute error (MAE) for DFT+D being 0.0099 Å^2 , while that for DFT is 0.0275 Å^2 . These amount to mean (absolute) relative errors (MARE) of about 12 and 34%, respectively. When comparing the DFT+D values with those from the X-ray diffraction data set, not all of the experimental values are underestimated and the MAE is smaller than that of the

Table 3

Selected simulated (DFT and DFT+D) and neutron diffraction U_{eq} values (Å²) for benzophenone at 70 and 300 K.

Note that at 70 K only a dispersion-correction DFT simulation was performed. The DFT values are calculated from the numerical ADPs as $U_{\text{eq}} = 1/3(U_{11} + U_{22} + U_{33})$. (See Fig. 1 for atom numbering.)

	DFT	DFT+D	Experiment
C1	0.0355 (1)	0.0493 (1)	0.0549 (7)
H1	0.0533 (1)	0.0703 (1)	0.083 (2)
C2	0.0461 (1)	0.0640 (1)	0.0687 (9)
H2	0.0751 (1)	0.0998 (1)	0.107 (3)
C6	0.0323 (1)	0.0435 (1)	0.0516 (7)
C7	0.0361 (1)	0.0486 (1)	0.0563 (7)
O	0.0629 (1)	0.0800 (1)	0.0875 (14)

	DFT	DFT+D	Experiment
C1	–	0.0093 (1)	0.0097 (2)
H1	–	0.0136 (1)	0.0246 (8)
C2	–	0.0123 (1)	0.0118 (3)
H2	–	0.0201 (1)	0.0295 (9)
C6	–	0.0080 (1)	0.0084 (2)
C7	–	0.0089 (1)	0.0087 (2)
O	–	0.0145 (1)	0.0152 (4)

neutron diffraction data at 0.0086 Å^2 . However, this is primarily due to some of the H-atom values being much smaller in the X-ray refinement than in the neutron refinement, most likely because of the constrained nature of the refinement.

Fig. 2 shows the experimental and DFT+D molecular structures at 300 K, with displacement ellipsoids plotted. Visual inspection confirms that the physical extent of the MD ADPs (*i.e.* the U_{eq} values) agree well with the experimental data. However, it is apparent that the orientations of some of the ellipsoids differ noticeably in some instances. The orientations of the ellipsoids are dictated by the U_{ij} , $i \neq j$, values, which are typically much smaller than the U_{ii} values. For example, from the 300 K neutron diffraction data, the values for C1 are $U_{11} = 0.066 (2) \text{ Å}^2$ and $U_{12} = -0.0009 (15) \text{ Å}^2$. The large uncertainty reflects the difficulty in determining these parameters at high temperature. From the DFT+D simulation, these values are $U_{11} = 0.0655 \text{ Å}^2$ and $U_{12} = -0.0015 \text{ Å}^2$. Generally, the DFT+D and neutron diffraction values agree qualitatively, with the differences between the neutron diffraction data and the heavy-atom X-ray values being of comparable magnitude to those between the neutron diffraction data and the DFT+D MD simulation. It is also clear from Fig. 2 that the DFT+D simulation correctly captures the overall rigid-body motion that dominates the experimental ADPs.

At 70 K the DFT+D MD U_{eq} values are again generally smaller than the experimental values. The overall MARE is larger, at 19%. However, there is a noticeable difference between the values for the heavy atoms and those for the H atoms, as can be seen in Table 3. For the C atoms alone the MARE is 3.1%, while for the H atoms it is 42%. A much

smaller difference is seen between the two sets of atoms at 300 K. The poor agreement for the H atoms is most likely a result of the classical nature of the MD simulation, which ignores the zero-point energy contributions that are particularly important for the lighter H atoms. Path-integral MD simulations are capable of capturing these effects (Reilly *et al.*, 2010*a*), even at very low temperatures (Reilly *et al.*, 2010*b*). However, the computational cost of such simulations is still generally prohibitive for DFT-MD simulations at 70 K. The good agreement for the C atoms likely stems from the fact that their motion is dominated by the low-frequency lattice vibrations, which are much better approximated by classical nuclear dynamics.

The total energy of the equilibrium DFT geometry is -3065.38 eV. The dispersion correction adds a further -2.60 eV. This is only 0.08% of the total energy of the DFT+D equilibrium structure but it makes a substantial difference to the dynamic behaviour of the system, which is governed by energy differences. While the dispersion correction clearly improves on the standard DFT picture of the thermal motion, there remain significant differences between the theoretical and experimental values. More robust DFT+D schemes, such as that of Tkatchenko & Scheffler (2009), might give better results, but a full treatment would require accounting for screening effects and many-body van der Waals interactions (Tkatchenko *et al.*, 2012), which is presently not possible in MD simulations.

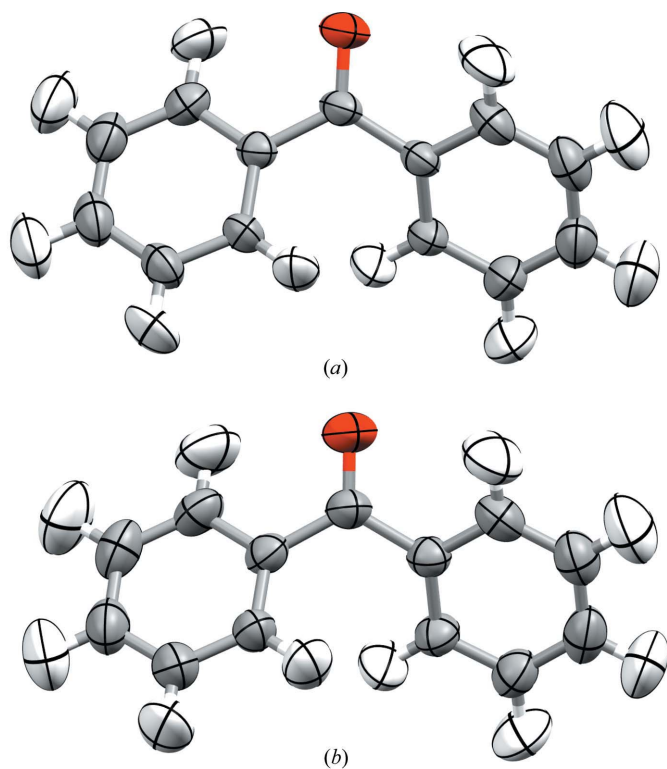


Figure 2
ADPs of benzophenone (50% probability level) determined at 300 K from (a) DFT+D MD simulations and (b) neutron diffraction. The orientation is the same as that in Fig. 1.

Table 4

Theoretical distance corrections (\AA) for a selection of bond lengths in benzophenone.

$\Delta r_{\text{MD}} = r_{\text{e,MD}} - r_{\text{a,MD}}$. Δr_{TLS} has been calculated using the program *PLATON* and the DFT+D ADPs (Spek, 2009). (See Fig. 1 for atom numbering.)

Distance	DFT	DFT+D	
	Δr_{MD}	Δr_{MD}	Δr_{TLS}
Δr C1–C2	0.0082	0.0076	0.0068
Δr C1–H1	0.0113	0.0122	0.0058
Δr C1–C6	0.0090	0.0203	0.0122
Δr C6–C7	0.0036	0.0050	0.0073
Δr C7–O	0.0135	0.0179	0.0108

3.3. Equilibrium crystal structure

Finally, we discuss the differences between the thermally and time-averaged structure of benzophenone in the DFT+D MD simulations at 300 K and the hypothetical vibration-free 0 K equilibrium DFT+D structure, and their relevance to the experimental structure. Benzophenone is, in principle, relatively rigid and the theoretical intramolecular distance corrections ($\Delta r = r_{\text{e,MD}} - r_{\text{a,MD}}$, where e and a denote the equilibrium and time-averaged structures, respectively) are likely to be reasonably small. It should therefore represent a system where the traditional TLS rigid-body approach should give good estimates for the corrections to bond lengths to account for thermal motion. Table 4 lists some of the corrections determined by the DFT and DFT+D simulations, as well as TLS distance corrections calculated using the theoretical DFT+D ADPs and mean positions. All three approaches show that thermal motion should shorten the bond length. The DFT+D corrections are typically larger than the DFT values, which makes sense in terms of the larger vibrational amplitudes observed in the DFT+D simulation. The TLS values are smaller in many cases than the values obtained directly from the DFT+D MD simulation and do not have the same relative trends as the DFT+D values.

How significant these corrections are depends on the final uncertainties in the experimental time-averaged distances. The MD results suggest that a structure at a lower temperature should have longer bond lengths than one at a higher temperature. Table 2 shows that, while in many cases the bond lengths are shorter at 300 K than at 70 K, there are some that are lengthened. This is not surprising, as the corrections are of the same order of magnitude as the uncertainties in the bond lengths. More accurate studies are of course possible and it is useful to have an idea of the magnitude of the effect of thermal motion on structures similar to benzophenone at room temperature, with the results here suggesting that bonded distances in rigid ring systems are barely affected by thermal motion.

The intramolecular distance corrections are small, in part because the motions of atoms relative to one another within a molecule are correlated. Significant changes in the positions of the atoms lead to only small corrections to bonded distances because the whole molecule shifts. Unlike rigid-body approaches, the MD simulations are capable of probing the

differences between mean and equilibrium positions and not just distances. In the DFT+D simulation at 300 K, the magnitude of the positional correction vectors ($\Delta\mathbf{r}_{\text{MD}}$) ranges between 0.02 and 0.21 Å, with the O atom, for example, shifting by 0.14 Å. This correction is much larger than the uncertainty in the position of the atom, leading to appreciable corrections to the intermolecular distances. As an example, $\text{O}\cdots\text{H2}^*$, where H2^* is related to H2 by the symmetry operation $(\frac{1}{2}-x, 1-y, -\frac{1}{2}+z)$, is 2.410 Å in the DFT equilibrium structure but 2.558 Å in the DFT+D MD time-averaged structure. The resulting difference of 0.148 Å is very large and significant, and highlights the ever-present difficulties in comparing time-averaged diffraction data with equilibrium structures from theory. In many cases, the standard practice for obtaining force fields involves matching static equilibrium geometries from theory with the time-averaged results of diffraction experiments. Fitting a force field in such a manner for benzophenone will not give a physically realistic or consistent model of the potential-energy surface of the crystal.

4. Conclusion

The structure of the stable α phase of benzophenone has been studied using DFT–MD simulations, and single-crystal neutron and X-ray diffraction at 70, 295 and 300 K. The DFT simulations were performed with and without an empirical correction for van der Waals forces. These forces represent long-range correlations of the electron density, which are poorly modelled by most mainstream DFT functionals. The dispersion correction significantly improves the agreement between the MD-derived displacement parameters and those from an anisotropic refinement of the experimental data at 300 K. Equilibrium corrections to positions and interatomic distances were derived from the MD simulations. The bonded-distance corrections are relatively small and comparable in size to rigid-body corrections, and are not significant in terms of the experimental uncertainties. However, the positional and intermolecular distance corrections are large and statistically significant. At 70 K, quantum mechanical effects, primarily zero-point energy, limit the usefulness of classical nuclear dynamics, but the heavy-atom U_{eq} values agree well with experiment and could be used with rigid-body methods to give representative H-atom ADPs.

It is clear from the present study that DFT has potential in predicting ADPs for comparison with, or even aiding the refinement of, experimental crystal structures. In the present work, the use of a van der Waals correction to the DFT functional has been essential. With the application of more sophisticated dispersion corrections for van der Waals interactions (Tkatchenko *et al.*, 2012), dispersion-corrected DFT should become a reliable tool for the prediction of high-temperature ADPs of molecular crystals.

The simulations were performed using the computational resources of the EPSRC National Service for Computational Chemistry (<http://www.nscs.ac.uk>) and HECToR, the UK's

national high-performance computing service, which is provided by UoE HPCx Ltd at the University of Edinburgh, Cray Inc. and NAG Ltd, and funded by the Office of Science and Technology through EPSRC's High End Computing Programme. Neutron beamtime on SXD at ISIS was provided by the STFC (Science and Technology Facilities Council). The authors gratefully acknowledge Dr Aziz Daoud-Aladine (ISIS) for assistance with initial neutron data collection. DAW acknowledges EPSRC for the award of a Career Acceleration Fellowship (EP/I004122).

References

- Allen, M. P. & Tildesley, D. J. (1989). *Computer Simulation of Liquids*. Oxford University Press.
- Baroni, S., de Gironcoli, S. & Dal Corso, A. (2001). *Rev. Mod. Phys.* **73**, 515–562.
- Blake, A. J., Brain, P. T., McNab, H., Miller, J., Morrison, C. A., Parsons, S., Rankin, D. W. H., Robertson, H. E. & Smart, B. A. (1996). *J. Phys. Chem.* **100**, 12280–12287.
- Brain, P. T., Morrison, C. A., Parsons, S. & Rankin, D. W. H. (1996). *J. Chem. Soc. Dalton Trans.* pp. 4589–4596.
- Criado, A., Conde, A. & Márquez, R. (1984). *Acta Cryst.* **A40**, 696–701.
- Dove, M. T. (2005). *Introduction to Lattice Dynamics*. Oxford University Press.
- Elstner, M., Hobza, P., Frauenheim, T., Suhai, S. & Kaxiras, E. (2001). *J. Chem. Phys.* **114**, 5149–5155.
- Fleischer, E. B., Sung, N. & Hawkinson, S. (1968). *J. Phys. Chem.* **72**, 4311–4312.
- Flyvbjerg, H. & Petersen, H. G. (1989). *J. Chem. Phys.* **91**, 461–466.
- Glykos, N. M. (2007). *Acta Cryst.* **D63**, 705–713.
- Goedecker, S., Teter, M. & Hutter, J. (1996). *Phys. Rev. B*, **54**, 1703–1710.
- Gossner, B. (1904). *Z. Kristallogr.* **38**, 110–168.
- Grimme, S. (2004). *J. Comput. Chem.* **25**, 1463–1473.
- Grimme, S., Antony, J., Ehrlich, S. & Krieg, H. (2010). *J. Chem. Phys.* **132**, 154104.
- Gutmann, M. J. (2005). *SXD2001*. ISIS Facility, Rutherford Appleton Laboratory, Oxfordshire, England.
- Hartwigsen, C., Goedecker, S. & Hutter, J. (1998). *Phys. Rev. B*, **58**, 3641–3662.
- Hoover, W. G. (1985). *Phys. Rev. A*, **31**, 1695–1697.
- Keen, D. A., Gutmann, M. J. & Wilson, C. C. (2006). *J. Appl. Cryst.* **39**, 714–722.
- Krack, M. (2005). *Theor. Chem. Acc.* **114**, 145–152.
- Kutzke, H., Klapper, H., Hammond, R. B. & Roberts, K. J. (2000). *Acta Cryst.* **B56**, 486–496.
- Lippert, G., Hutter, J. & Parrinello, M. (1997). *Mol. Phys.* **92**, 477–487.
- Madsen, A. Ø. (2006). *J. Appl. Cryst.* **39**, 757–758.
- McCaffrey, P. D., Mawhorter, R. J., Turner, A. R., Brain, P. T. & Rankin, D. W. (2007). *J. Phys. Chem. A*, **111**, 6103–6114.
- Mitzel, N. W. & Rankin, D. W. H. (2003). *Dalton Trans.* pp. 3650–3662.
- Moncol, J. & Coppens, P. (2004). Private communication (deposition number 245188). CCDC, Union Road, Cambridge, England.
- Nosé, S. (1984). *J. Chem. Phys.* **81**, 511–519.
- Perdew, J. P., Burke, K. & Ernzerhof, M. (1996). *Phys. Rev. Lett.* **77**, 3865–3868.
- Pilati, T., Demartin, F. & Gramaccioli, C. M. (1998). *Phys. Chem. Miner.* **26**, 149–155.
- Reilly, A. M., Habershon, S., Morrison, C. A. & Rankin, D. W. H. (2010a). *J. Chem. Phys.* **132**, 134511.
- Reilly, A. M., Habershon, S., Morrison, C. A. & Rankin, D. W. H. (2010b). *J. Chem. Phys.* **132**, 094502.

- Reilly, A. M., Morrison, C. A. & Rankin, D. W. H. (2011). *Acta Cryst.* **A67**, 336–345.
- Reilly, A. M., Morrison, C. A., Rankin, D. W. H. & McLean, K. R. (2011). *Acta Cryst.* **A67**, 346–356.
- Reilly, A. M., Wann, D. A., Morrison, C. A. & Rankin, D. W. H. (2007). *Chem. Phys. Lett.* **448**, 61–64.
- Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* **B24**, 63–76.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sipachev, V. A. (1985). *J. Mol. Struct. (Theochem)*, **121**, 143–151.
- Sipachev, V. A. (2000). *Struct. Chem.* **11**, 167–172.
- Sipachev, V. A. (2001). *J. Mol. Struct.* **567**, 67–72.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Tkatchenko, A., DiStasio, R. A. Jr, Car, R. & Scheffler, M. (2012). *Phys. Rev. Lett.* **108**, 236402.
- Tkatchenko, A. & Scheffler, M. (2009). *Phys. Rev. Lett.* **102**, 073005.
- VandeVondele, J., Krack, M., Mohamed, F., Parrinello, M., Chassaing, T. & Hutter, J. (2005). *Comput. Phys. Commun.* **167**, 103–128.
- Wann, D. A., Less, R. J., Rataboul, F., McCaffrey, P. D., Reilly, A. M., Robertson, H. E., Lickiss, P. D. & Rankin, D. W. H. (2008). *Organometallics*, **27**, 4183–4187.
- Wann, D. A., Zakharov, A. V., Reilly, A. M., McCaffrey, P. D. & Rankin, D. W. (2009). *J. Phys. Chem. A*, **113**, 9511–9520.
- Whitten, A. E. & Spackman, M. A. (2006). *Acta Cryst.* **B62**, 875–888.
- Williams, R. W. & Malhotra, D. (2006). *Chem. Phys.* **327**, 54–62.