A critical analysis of dipole-moment calculations as obtained from experimental and theoretical structure factors

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A critical analysis of dipole-moment calculations as obtained from experimental and theoretical structure factors

Agnieszka Poulain-Paul, Ayoub Nassour, Christian Jelsch, Benoit Guillot, Maciej Kubicki and Claude Lecomte*

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Three models of charge-density distribution – Hansen–Coppens multipolar, virtual atom and kappa – of different complexities, different numbers of refined parameters, and with variable levels of restraints, were tested against theoretical and high-resolution X-ray diffraction structure factors for 2-methyl-4-nitro-1-phenyl-1H-imidazole-5-carbonitrile. The influence of the model, refinement strategy, multipole level and treatment of the H atoms on the dipole moment was investigated. The dipole moment turned out to be very sensitive to the refinement strategy. Also, small changes in H-atom treatment can greatly influence the calculated magnitude and orientation of the dipole moment. The best results were obtained when H atoms were kept in positions determined by neutron diffraction and anisotropic displacement parameters (obtained by SHADE, in this case) were used. Also, constraints on kappa values of H atoms were found to be superior to the free refinement of these parameters. It is also shown that the over-parametrization of the multipolar model, although possibly leading to better residuals, in general gives worse dipole moments.

1. Introduction

The extraction of reproducible and reliable electrostatic properties from a charge-density analysis is a key issue in assessing the physical reliability of experimental diffraction data refinement. The multipolar modelling may be influenced by many factors, such as diffraction data quality, thermal smearing or correlations between refined parameters. Even if the electron density is statistically well fitted to the experimental data in the process of refinement, the resulting atomic and molecular properties, for example electrostatic potential, dipole moments ($\mu$) and interaction energies, can be questionable due to the lack of physical constraints (Spackman, 1992; Coppens, 1997; Pérès et al., 1999; Volkov et al., 2001; Spackman et al., 2007; Domagala & Jelsch, 2008 and references therein). Several attempts were made to test various electron-density models, available pseudoatom databases (Durka et al., 2010; Bał et al., 2011) or the influence of constraints on the electrostatic properties. Using experimental and theoretical data (Abramov et al., 1999; Volkov et al., 2000), it was found, for instance, that the large differences between $\mu$ values observed between multipolar and integrated atom-in-molecules (AIM) (Bader, 1990) methods may be caused by the partitioning method rather than by the differences in charge distribution, choice of the multipole model – unrestricted or $\kappa$-restricted (Volkov et al., 2000) – or by the order of multipoles. On the other hand, the dipole moments in crystals derived from multipolar refinements of X-ray data are generally found to be larger than those calculated ab initio for the molecule in vacuo, due to induced polarization. An increase has also been observed in comparison with the values obtained from theoretical calculations (Abramov et al., 1999).

For the last ten years, we have been investigating the charge-density distribution of a series of nitroimidazole derivatives (Kubicki et al., 2002; Paul, Kubicki, Jelsch et al., 2011; Paul, Kubicki, Kubas et al., 2011). In this last paper (Paul, Kubicki, Kubas et al., 2011) large discrepancies were observed between the dipole moment of 2-methyl-4-nitro-1-phenyl-1H-imidazole-5-carbonitrile [compound (I), Fig. 1] calculated from theoretical and experimental data. The theoretical calculations were performed for a single molecule of (I) (B3LYP+$\omega$D, $\mu$ = 9.68 D) and using a conductor-like screening model (COSMO, $\mu$ = 12.4 D, with the dielectric constant $\varepsilon$ set to infinity to mimic the screening of the electrostatic moments in the crystal). The moment derived from experimental diffraction data using the multipolar Hansen–Coppens model was 25.7 D.

The magnitude of the dipole moment obtained from experiment was much higher than that derived from theoretical diffraction data. Furthermore, this dipole moment was found to be extremely dependent on the refinement strategy, which is not the case, for example, when comparing topological

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2.2. Refinement versus theoretical structure factors – charge-density models

2.2.1. Multipolar Hansen–Coppens model (MM\textsubscript{theo}).

Multipolar refinement was performed using the Hansen–Coppens (Hansen & Coppens, 1978) model implemented in the MoPro package (Guillot et al., 2001; Jelsch et al., 2005). The pseudoatom electron density is described by
\[
\rho_{\text{atom}}(r) = \rho_{\text{core}}(r) + P_{\text{val}} \kappa^3 \rho_{\text{val}}(kr) + \sum_l \kappa^3 R_l(\kappa r) \sum_{nm} P_{lmn}(\theta, \varphi),
\]

where the first two terms are the spherically averaged core and valence electron densities of the atom, and the last term corresponds to expansion/contraction of the non-spherical valence density in terms of real spherical harmonic functions. \( P_{\text{val}} \) is the valence population, \( P_{lmn} \) are the multipole populations, and \( \kappa \) and \( \kappa' \) are the contraction/expansion parameters. \( R_l \) is a radial Slater-type function:

\[
R_l(r) = \frac{\xi_l^n}{(n_l + 2)!} r^{n_l} \exp(-\xi_l r), \quad n_l \geq l.
\]

The O, C and N atoms were refined up to octupole or hexavalence density in terms of real spherical harmonic functions. The last term in equation (1) is eliminated, i.e. \( \kappa = 0 \) for all tests; and \( \kappa \) (H atoms) or \( \kappa \) (non-H atoms) were set to zero. The virtual-atom model (VIR theo) was defined by Pillet et al. (2001) in the test study on multipole refinement against theoretical corundum structure factors which accounted for the difference between DFT and Hartree–Fock (HF) core densities. Therefore Tables 1–3 present the results including a \( \kappa_{\text{core}} \) refinement, whereas Table S1 in the supplementary material gives the results with a scale-factor refinement.

Different orders of multipolar expansion were tested along with optimal restraints on symmetry and similarity of chemically equivalent atoms as recently determined in free-R-factor calculations (Paul, Kubicki, Kubas et al., 2011); constraints on \( \kappa \) H atoms (default value 1.16; Stewart et al., 1965) were also tested.

2.2.2. Virtual-atom model (VIRtheo). The virtual-atom model (Dadda et al., 2012) introduces a simplification in the multipolar model and was designed by us to be routinely used in macromolecular modelling. This approach describes the electron density as a superposition of real and virtual spherical atoms:

\[
\rho(r) = \sum_{\text{atom}} [\rho_{\text{atom}}^\text{core}(r) + P_{\text{val}}^\text{atom} \kappa^3 \rho_{\text{val}}^\text{atom}(kr)] + \sum_{\text{vir}} P_{\text{vir}} \kappa^3 \rho_{\text{vir}}^\text{vir}(kr),
\]

where \( \rho_{\text{core}} \) and \( \rho_{\text{val}} \) are the core and spherical valence electron densities that can be calculated from HF or DFT methods. The real atoms (C, O, N, H) have a spherical symmetry and are described by the first and second terms of equation (3). The third term corresponds to the deformation electron density \( \rho_{\text{vir}} \) generated by the additional virtual atoms, which take asphericity into account. In this approach, the last term in equation (1) is eliminated, i.e. all multipolar populations are reduced to monopoles and additional virtual spherical atoms are initially placed on the positions of covalent bonding electron density and of electron lone pairs (with a starting monopole value \( P_{\text{val}} = 0 \)).

A similar point-charge model has already been applied in a few cases in the literature: it was reported for urea (Scheringer, Kutoglu et al., 1978; Scheringer, Mullen et al., 1978; Mullen & Hellner, 1978a), thiourea (Scheringer, Kutoglu et al., 1978; Scheringer, Mullen et al., 1978; Mullen & Hellner, 1978b), diborane (Mullen & Hellner, 1977; Scheringer, Mullen & Hellner, 1978), decaborane (Dietrich et al., 1979), cyanuric acid (Dietrich et al., 1979) and silicon (Scheringer, 1980). More recently, a bond scatterers model was applied by Alfonine et al. (2004, 2007) for ultra-high-resolution protein refinement.

There is an automatic procedure in the software MoPro (Jelsch et al., 2005) which allows one to generate the coordinates of such virtual atoms as well as the restraints/constraints being applied on their geometries. The virtual atoms generated by MoPro are depicted in Fig. 2 as green spheres. The \( Q_{AB} \) and \( Q_{LP} \) virtual atoms refer, in this paper, to the bonding density between atoms \( A \) and \( B \), and to the charge located on the expected oxygen lone-pairs site, respectively.

In this approximation, all atoms (real and virtual ones) have spherical symmetry. Refinement against the theoretical data concerns therefore only spherical \( \kappa \) coefficients and \( P_{\text{val}} \) in the structure factor calculation.
valence populations of all atoms (using an electroneutrality constraint), and the coordinates of virtual atoms. Up to now, only one type of virtual atom is available, the electron density of which, $\rho_{\text{va}}(r)$, was fitted using Slater functions from a Fourier residual density computed using theoretical structure factors and after a spherical atoms (independent-atom model) refinement. For this purpose, a centrosymmetric crystal of $\beta\lambda$-histidine (Coppens et al., 1999) was selected and the theoretical structure factors were computed from ab initio calculations. The residual density was fitted in a [0.1, 1] Å interval around the $\text{Ca} - \text{C} \beta$ bonding electron-density peak of the amino acid in the plane perpendicular to the $\text{Ca} - \text{C} \beta$ bond to avoid effects of the neighbouring C atoms. The Slater function coefficients and $\rho_{\text{va}}(r)$ curve are shown in Datta et al. (2012).

Models with different levels of restraints on the charge density (e.g. chemical similarity) imposed only on the virtual atoms or also on real atoms were tested. The default stereochemical restraints include linearity (the virtual-atom position is restrained to stay on the line connecting two bonded atoms), distances, planarity and similarity of angles. Soft linearity restraints ($\sigma = 0.1$ Å) were applied because of a lack of convergence in calculations using stronger restraints. The lone-pairs ($\text{N} - \text{O} - \text{Lp} \simeq \text{N} - \text{O} - \text{Lp}'$) angle similarity constraint was removed for the NO$_3$ group to take into account the high peaks of positive electron density in the Fourier residual maps on both sides of each O atom. An additional virtual atom was introduced on the N=O bonds, close to the O atom (Fig. 2), to reduce the high negative residual density peak located on the bond. To compare the results with and without these additional atoms, see Table S4 in the supplementary material.

To reduce the number of least-squares variables of the refinement, geometrical and chemical equivalences were applied to the corresponding virtual and real atoms (see footnotes to Table 3).

### 2.2.3. Kappa model (KM$_\text{theo}$)

In the kappa model proposed by Becker and Coppens (Coppens et al., 1979), the total electron density of an atom is defined by

$$\rho_{\text{atom}}(r) = \rho_{\text{core}}(r) + P_{\text{va}}\kappa^3\rho_{\text{va}}(\kappa r),$$

where $P_{\text{va}}$ is the valence population and $\kappa$ is the spherical expansion/contraction coefficient. This model is simpler than the multipolar and the virtual-atom models, as the charges are attributed only to the real atoms and no aspherical deformation electron density is considered.

Coppens et al. (1979) were able to obtain reasonable values of the atomic charges and dipole moments for organic and inorganic compounds using this approximation for experimental and theoretical data, when comparing them with more sophisticated methods.

### 2.3. Refinements based on experimental data

The experimental details of the single-crystal diffraction may be found in Paul, Kubicki, Kubas et al. (2011). Refinements based on the experimental data were performed using the same three electron-density models (MM, VIR and KM) as for the theoretical data; however additional parameters, such as ADPs and coordinates, were refined knowing that the lack of special precautions (especially in the case of H atoms) can lead to wrong conclusions. The residual maps did not show any evidence that could suggest refining of any $\kappa_{\text{core}}$ parameters for experimental data.

#### 2.3.1. Multipolar model (MM$_\text{exp}$)

$R_{\text{free}}$, restraints as defined in Paul, Kubicki, Kubas et al. (2011) were kept constant and various multipolar expansion levels for H and non-H atoms were tested. In models 4$c$ and 4$f$, according to the theoretical fit (see below), hexadecapoles were refined for the cyano-group atoms (C91 and N91) as the bond charge concentration is quite significant, while the other non-H atoms were kept at the octupolar level.

As more parameters were refined compared to the theoretical models ($xyz$ and $U_{ij}$), only restrained refinements were tested to avoid possible charge-density parameter correlations, which could influence the electrostatic properties. Details of the restraints used are given in the supplementary material. The high/low-order refinements were performed to obtain reliable parameters for the H atoms as no neutron data were available. High-order refinements were performed for $xyz$ and $U_{ij}$ of non-H atoms followed by low-order refinement of positions and isotropic displacement parameters of H atoms, and then H-atom positions were moved to neutron distances. Then the ADPs of H atoms were estimated using the SHADE2.1 server (Madsen, 2006), and their $\kappa$ and $k'$ parameters were, respectively, restrained to 1.16 and 1.25 ($\sigma_i = 0.01$), which were found to be the best values after the theoretical structure-factor refinement. The H-atom positions and ADPs were refined in the last cycle [with constrained neutron distances and restraints on the ADPs, $U_{ij} \leq U_{ij}$ (SHADE) with $\sigma = 0.005$ for $U_{11}, U_{22}, U_{33}$ and $\sigma = 0.0005$ for $U_{12}, U_{23}, U_{13}$] to avoid their correlations with $\kappa$ and $P_{\text{va}}$, as some difficulties were already observed for the theoretical data refinement. For comparison, the results for models using H-atom ADPs constrained to SHADE are also presented. It will be shown that the H-atom treatment, i.e. the choice of $\kappa$ and refinement of ADPs, as well as the choice of the order of...
multipolar expansion, has a great influence on the dipole moment.

2.3.2. Virtual-atom model (VIR$_{\text{exp}}$). In the VIR$_{\text{exp}}$ model (Dadda et al., 2012), the calculations were performed based on the geometry obtained after high/low-order refinement of experimental data. The H atoms were moved to the neutron positions and refined with these H—X distances constrained in the final cycles, i.e. the H—X direction was refined at constant bond length. The ADPs of H atoms were obtained from SHADE and either refined with the same restraints as above for MM$_{\text{exp}}$ just before the final cycles of refinement for models 5a—5d, or kept constrained. For models 5e—5h the $\sigma$ of restrained H-atom ADPs was reduced by a factor of 5, due to unrealistic ellipsoids obtained with initial values. ADPs of the bond virtual atoms were constrained to the average values of the two neighbours. For the lone pairs, the ADPs were constrained to ride on the refined value of the carrying atom. At first, valence populations and $\kappa$ of all atoms were refined, followed by the virtual-atom positions. Then the refinement of ADPs and $xyz$ of all real non-H atoms was performed. The additional negative virtual atoms on the N=O bonds were implemented, even if not deemed necessary. The density was already well described with one virtual atom on this bond, but the comparison with the theoretical results would not be consistent.

2.3.3. Kappa model (KM$_{\text{exp}}$). The kappa model is obtained by setting the multipoles of atoms to zero. The final geometry from the multipolar refinement is kept, with no further refinement of coordinates and thermal motions, while the $P_{\text{val}}$ parameters of all atoms and $\kappa$ of non-H atoms are refined until convergence.

Besides the multipolar geometry, the virtual geometry was also tested. This second geometry is the same as in VIR$_{\text{exp}}$, i.e. geometry after high/low-order refinement, with H atoms moved to the neutron H—X distances and with their ADPs generated by SHADE.

It appeared that any attempts to refine the geometry obtained after high/low-order refinement (virtual geometry), including $xyz$ and ADPs or not, resulted in dipole-moment magnitudes close to the theoretical ones, but the directions were always incorrect. In contrast, for the multipolar geometry, the directions were close to the multipolar dipole moment. Therefore the multipolar geometry was chosen for further kappa-refinement tests.

2.4. Dipole-moment calculations

The molecular dipole moments $\mu$ are calculated with the origin at the centre of mass, based on atomic net charges and atomic dipoles, according to the formula

$$\mu_{\text{total}} = \sum_i \mu_i + \sum_i r_i q_i.$$  \hfill (5)

Owing to the electroneutrality constraint, $\mu$ is actually independent of the origin. The atomic dipole-moment contributions are dependent on eight variables: the net charge derived from $P_{\text{val}}$, the $\kappa$ parameter, the coordinates and the three dipole populations $P_{10}$, $P_{11+}$ and $P_{11-}$. Only dipolar terms in the multipole expansion contribute to the dipole moment (Coppens, 1997).

3. Results

The dipole-moment magnitudes obtained with DFT methods at the B3LYP/6-31G(d,p) level of theory are 9.17 D for a single molecule and 10.61 D for the periodic system using a Bader AIM partitioning (Bader, 1990); this latter value can be taken as a reference to rank the calculations based on theoretical structure factors. This reference is not strictly valid for the experimental data because no experimental dipole measurement is available.

As the coordinates and ADPs were not refined against theoretical data, the correlations between the refined parameters, that have an impact on the total dipole moment, are small compared to experimental data.

3.1. Multipolar refinements against theoretical structure factors (MM$_{\text{theo}}$)

Of the numerous refinements performed, 12 are reported in Table 1 (models 1a—1l). The varied parameters are: (a) order of multipolar expansion of H and non-H atoms; (b) $\kappa_{\text{hyd}}$ refined or constrained to 1.16; (c) $R_{\text{free}}$ restraints applied or not on the symmetry and similarity of the charge distribution of equivalent atoms.

As expected, the crystallographic agreement factors are better for models with more parameters refined. The goodness of fit at the convergence should be close to zero for theoretical data (unit weighting schemes) rather than unity for the experimental refinements (Moss et al., 1995). The quality of refinements is confirmed by the Fourier residual and static electron-density maps (Fig. S2); the largest residual electron densities ($0.20$—$0.25$ e Å$^{-3}$) are related to the high resolution used for calculations ($s = 1.2$ Å$^{-1}$). With an $s \leq 1.0$ Å$^{-1}$ resolution cutoff, all these residual electron-density values drop by $\sim 0.1$ e Å$^{-3}$ for models 1a—1h and by 0.05 e Å$^{-3}$ for models 1i—1l, for both positive and negative peaks. This residual electron density is spread over the molecule in the regions of heteroatomic bonds. It is important to note that the multipolar model works much better when describing the bonding electron density between atoms of the same type (C—C bonds, for example). This is related to the radial expansion parameters (Moss et al., 1995).

As shown in Table 1, the dipole-moment magnitudes range between 13.3 D (refinement 1f) and 10.1 D (refinement 1i) compared to the expected 10.6 D theoretical value. The direction of the moment can be described by the difference between the vector calculated in CRYSTAL09 and the $\mu$ vector from the appropriate refinement. The difference angle varies from 12.6° (1a) to 14.7° (1l). This angular dispersion is small, as also shown in Fig. 3, and the systematic angular difference is surprising; it may be related to the partitioning used for the theoretical dipole-moment calculation in the solid state (AIM method). The MM$_{\text{theo}}$ dipole moments are larger than the theoretical one (10.6 D) for models using hexadeca-
polar functions for all non-H atoms and quadrupoles for H atoms. Compared to theory, the closest values of the dipole-moment magnitudes are obtained for models 1i–1l, with octupole/dipole non-H/H-atom treatment and with hexadecapolar description of the very electron-rich cyano atoms, whatever the type of restraints.

The directions of selected total dipole moments and their components (contributions from atomic dipoles and monopole charges) are depicted in Fig. 3 (all models are deposited as Figs. S3–S4). The contribution from the atomic dipoles is constantly larger in models with higher multipolar expansion (see also Table 1) but the maximal difference (1e–1g) is only 1.16 D. For the \( \mu \) derived from the monopole charges, the maximal difference is 2.31 D (1b–1k). It results in a maximum difference for the total \( \mu \) of 3.14 D between models 1f and 1c, i.e. more than 25%.

In general, the following factors increase the dipole-moment modulus:

(a) Multipole expansion: a higher order of multipolar expansion of H atoms (quadrupolar) and non-H atoms (hexadecapolar) leads to higher \( \mu \). This is also noticed for the experimental data, where models with OCT\_mon/DIP\_HYD are analysed. Nevertheless, most quadrupolar terms of hydrogen expansion are not statistically significant (at the 5/2 level), except the \( 2z^2 - (x^2 + y^2) \) quadrupole along the H—X axis. In fact, refinement with only significant quadrupoles (HYD) and hexadecapoles (NOH) lowers the \( \mu \) values in models 1a, 1b, 1e and 1f by 3.9, 0.54, 3.5 and 0.60%, respectively, with no changes in \( R \)-factor statistics. The great impact of the H atoms may be due to their location at the opposite side of the molecule with respect to the electronegative nitro and cyano groups.

(b) \( \kappa\_hyd \) refinement: the models with refined \( \kappa\_hyd \) give slightly higher values of dipole moments (average \( +1.0\% \) of

---

**Table 1**

<table>
<thead>
<tr>
<th>Model</th>
<th>Multipolar order non-H/H</th>
<th>( \kappa_hyd )</th>
<th>No. of variables</th>
<th>Restraints applied</th>
<th>RF, ( wR2F ) (%)</th>
<th>Goof</th>
<th>( \mu ) total (monopoles/dipoles) (D)</th>
<th>( \mu ) total (monopoles/dipoles) (D) only for significant HEX/QUA</th>
<th>Angle between ( \mu_calc ) and ( \mu_obs ) vectors</th>
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</thead>
<tbody>
<tr>
<td>1a</td>
<td>HEX/QUA refined</td>
<td>534</td>
<td>0.421</td>
<td>0.051</td>
<td>12.11 (11.26/2.48)</td>
<td>11.64 (10.80/2.60)</td>
<td>12.6</td>
<td></td>
<td></td>
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<tr>
<td>1b</td>
<td>HEX/QUA</td>
<td>534</td>
<td>0.424</td>
<td>0.052</td>
<td>13.02 (12.22/2.37)</td>
<td>12.95 (12.17/2.40)</td>
<td>13.0</td>
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<td></td>
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<tr>
<td>1c</td>
<td>OCT/DIP refined</td>
<td>341</td>
<td>0.505</td>
<td>0.066</td>
<td>10.71 (10.90/1.57)</td>
<td>13.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>OCT/DIP</td>
<td>341</td>
<td>0.513</td>
<td>0.068</td>
<td>11.11 (10.76/1.43)</td>
<td>13.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1e</td>
<td>HEX/QUA refined</td>
<td>534</td>
<td>( R_free )</td>
<td>0.433</td>
<td>12.42 (11.12/2.50)</td>
<td>11.98 (10.67/2.52)</td>
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<tr>
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<td>HEX/QUA</td>
<td>534</td>
<td>( R_free )</td>
<td>0.435</td>
<td>13.28 (12.02/2.43)</td>
<td>13.21 (11.96/2.38)</td>
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<tr>
<td>1g</td>
<td>OCT/DIP refined</td>
<td>341</td>
<td>( R_free )</td>
<td>0.514</td>
<td>11.00 (10.56/1.34)</td>
<td>11.45 (10.00/1.23)</td>
<td>14.2</td>
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<tr>
<td>1h</td>
<td>OCT/DIP</td>
<td>341</td>
<td>( R_free )</td>
<td>0.521</td>
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<td>11.59 (10.20/1.31)</td>
<td>14.3</td>
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<td>1i</td>
<td>OCT and HEX (C_N)/DIP</td>
<td>359</td>
<td>0.501</td>
<td>0.065</td>
<td>10.14 (10.32/2.34)</td>
<td>10.73 (10.10/2.28)</td>
<td>13.2</td>
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<td></td>
</tr>
<tr>
<td>1j</td>
<td>OCT and HEX (C_N)/DIP</td>
<td>359</td>
<td>0.509</td>
<td>0.067</td>
<td>10.58 (10.27/2.26)</td>
<td>11.00 (10.16/2.18)</td>
<td>14.0</td>
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<tr>
<td>1k</td>
<td>OCT and HEX (C_N)/DIP</td>
<td>359</td>
<td>( R_free )</td>
<td>0.509</td>
<td>10.32 (9.91/2.14)</td>
<td>10.91 (9.52/2.03)</td>
<td>14.5</td>
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<tr>
<td>1l</td>
<td>OCT and HEX (C_N)/DIP</td>
<td>359</td>
<td>( R_free )</td>
<td>0.558</td>
<td>10.87 (10.67/2.22)</td>
<td>11.59 (10.32/2.15)</td>
<td>14.7</td>
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</tbody>
</table>

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**Figure 3**

Dipole-moment directions (grey, total; red, contribution from atomic dipoles; blue, contribution from atomic charges) for selected models 1a and 1g.
difference) compared to those with $\kappa_{\text{hyd}}$ fixed to 1.16. Nevertheless all these differences are within 3σ.

(c) $R_{\text{free}}$ restraints: the application of soft $R_{\text{free}}$ restraints for the current charge-density analysis does not influence significantly the $P_{\text{val}}$ values, compared to the unrestrained refinement.

As expected, the lowest H-atom valence populations are connected with the highest corresponding $\kappa_{\text{hyd}}$. The average $P_{\text{val, hyd}}$ in both 1c and 1g is 0.86 e ($\kappa = 1.19$), while in 1a and 1e it is 0.93 e ($\kappa = 1.15$). In models with constrained $\kappa_{\text{hyd}}$, $P_{\text{val}}$ has intermediate values. For non-H atoms, the largest differences are found for the C–N atoms [$P_{\text{val}}$(C91) = 4.53 (1) (1a, 1b, 1e)]

Figure 4
Multipolar electron density for atom C91 (left), N91 (middle) and the complete C–N group (right). The contribution of the different multipole levels is shown. Model 1a, lines 1–4: HEX, OCT, QUA and DIP. Model 1c, lines 5–7: OCT, QUA and DIP. Contour levels are ±0.05 e Å⁻³ for the DIP and QUA, and ±0.005 e Å⁻³ for the OCT and HEX contributions.
Table 2
Topological characteristics of the bond critical points for the C=N group in models 1a and 1c.

<table>
<thead>
<tr>
<th>cp</th>
<th>Atom 1</th>
<th>Atom 2</th>
<th>$D_{12}$ ($\AA$)</th>
<th>$D_{12g}$ ($\AA$)</th>
<th>$D_{22g}$ ($\AA$)</th>
<th>$\rho_{cp}$ (e Å$^{-3}$)</th>
<th>$\nabla^2 \rho$ (e Å$^{-5}$)</th>
<th>$\lambda_1$ (e Å$^{-5}$)</th>
<th>$\lambda_2$ (e Å$^{-5}$)</th>
<th>$\lambda_3$ (e Å$^{-5}$)</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model 1a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>cp1</td>
<td>C9</td>
<td>C91</td>
<td>1.4110</td>
<td>0.6798</td>
<td>0.7314</td>
<td>1.94</td>
<td>$-15.6$</td>
<td>$-13.4$</td>
<td>$-12.2$</td>
<td>10.0</td>
<td>0.09</td>
</tr>
<tr>
<td>cp2</td>
<td>C91</td>
<td>N91</td>
<td>1.1580</td>
<td>0.4029</td>
<td>0.7511</td>
<td>3.23</td>
<td>$-13.5$</td>
<td>$-25.7$</td>
<td>$-25.4$</td>
<td>37.6</td>
<td>0.01</td>
</tr>
<tr>
<td>Model 1c</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>cp1</td>
<td>C9</td>
<td>C91</td>
<td>1.4110</td>
<td>0.6890</td>
<td>0.7220</td>
<td>1.91</td>
<td>$-14.0$</td>
<td>$-13.2$</td>
<td>$-11.5$</td>
<td>10.7</td>
<td>0.13</td>
</tr>
<tr>
<td>cp2</td>
<td>C91</td>
<td>N91</td>
<td>1.1580</td>
<td>0.4070</td>
<td>0.7510</td>
<td>3.22</td>
<td>$-14.1$</td>
<td>$-24.9$</td>
<td>$-24.9$</td>
<td>35.7</td>
<td>0.00</td>
</tr>
</tbody>
</table>

1f) and 4.35 (1) e (1c, 1d, 1g, 1h), $P_{val}$ (N91) = 4.68 (1) (1a, 1b, 1c, 1f) and 4.82 (1) e (1c, 1d, 1g, 1h]), and for the methyl carbon atom, which is influenced by the valence population changes of its H atoms. The low H71, H72 and H73 $P_{val}$ values in 1c and 1g are in line with a higher C71 $P_{val}$.

(d) Atomic dipole contributions: for the H atoms, the only significant dipole is $P_{10}$, along the C–H bond direction. The lowest atomic $\mu_{dip}$ (atomic dipole contributions only) occur in 1c and 1g (H dipole expansion with $\kappa_{hyd}$ refined), whereas the highest $\mu_{dip}$ is obtained with H quadrupolar expansion.

For non-H atoms, the highest $\mu_{dip}$ are found on the two electronegative groups (C=N and NO$_2$). The C91 and N91 dipoles are significant along the triple bond, according to their cylindrical symmetry. The C91 $P_{10}$ value is $-0.385$ (2) in the HEX/QUA model and 0.310 (6) in OCT/DIP. For N91, $P_{10}$ is $-0.133$ (1) in the HEX/QUA model and $-0.119$ (1) in the OCT/DIP. The most significant atomic dipoles in the nitro group are the following: $P_{11s}$ [N8: $-0.027$ (3), O81 = O82: $-0.116$ (1) for HEX/QUA; and N8: $-0.021$ (3), O81 = O82: $-0.115$ (2) for OCT/DIP].

Fig. 4 compares all C=N atomic multipolar contributions for models 1a and 1c, for which the discrepancies between the C=N atoms’ valence populations are the highest. Whereas the quadrupolar terms are statistically equal, the dipolar contributions change considerably when hexadecapoles are added. Fig. 5 gives the static deformation and Laplacian maps of the C=N group for both 1a and 1c refinements and Table 2 lists the associated topological properties. All the electron-density features are similar within the standard deviation. Therefore, augmenting the order of the multipole extension greatly affects the dipole contribution to the dipole moment without changing the electron-density topology. Over-parametrization must therefore be avoided, especially for such a calculation.

In conclusion, the hexadecapolar expansion of atoms not belonging to the cylindrical C=N group is unnecessary for a thorough estimation of the dipole moment from theoretical structure-factor refinement. The same applies to the quadrupolar expansion for H atoms (see the results of refinement with only significant HEX/QUA populations – last column in Table 1).

Finally, when the scale factor is refined instead of $\kappa_{core}$, an increase in the dipole moment of 2.5 D is observed, almost exclusively due to a higher contribution of the atomic charges (see Table 1 and Table S1 in the supplementary material). On average the $\mu_{monopole}/\mu_{dipole}$ ratio is 7.6 for models where the scale factor is refined (models 1m–1t) and 5.5 for models with $\kappa_{core}$ refined (see Table 1 and Table S1 in the supplementary material).

The crystallographic statistics, dipole-moment vectors and values of all discussed parameters are given in Table S2 in the supplementary material.

Some attempts were also made to refine the multipolar model only to a dipolar expansion for all atoms, but the refinements were not stable, due to $\kappa'$ fluctuation of strongly electronegative groups, and no convergence was achieved.

3.2. Virtual-atom theoretical model (VIRtheo)

Two additional positive virtual atoms had to be introduced on the N=O bonds in the nitro group (Fig. 2), as a single virtual atom did not describe all the theoretical deformation density in this region. This addition modelled the negative N=O electron-density peak of 0.32 e Å$^{-3}$ (Fig. 6).

Nine different virtual-atom models were tested with the following variables: $\kappa_{hyd}$ (1.10, 1.13 and 1.16) and chemical equivalence restraints or constraints (Table 3). All nine models describe quite well the electron-density distribution (Fig. 6) – the static deformation maps are in good agreement with those obtained from MM$^{\text{theo}}$. However, the crystallographic agreement factors are systematically doubled.
compared to MM\textsubscript{theo}, as shown also by the residual maps (Fig. 6), a result in agreement with Dadda \textit{et al}. (2012).

Restriction of $\kappa_{\text{hyd}}$ was found to be crucial in limiting the influence of peripheral H atoms in the dipole-moment magnitude (models 2$j$–2$l$ in Table S3). Freely refined $\kappa_{\text{hyd}}$ values range between 1.19 and 1.26, leading to a too large dipole moment $17.3 < \mu < 18.7$ D.

As shown in Table 3, the dipole-moment magnitude dispersion is small compared to MM\textsubscript{theo}. The magnitude of $\mu$ is in particularly good agreement with that computed directly from theory for $\kappa_{\text{hyd}} = 1.13$ and it is not influenced by the charge-density similarity restraints or constraints. Hence, parallel trends are observed among models 2$a$–2$c$, 2$d$–2$f$ and 2$g$–2$i$: when $\kappa_{\text{hyd}}$ increased by 0.03, $\mu$ increases on average by 1.4 D (Fig. 7). Increasing $\kappa_{\text{hyd}}$ is also directly related to H-atom valence populations, but the non-H $\kappa$ coefficients remain rather stable (variation <1%) as for the virtual atoms (in general +2 to +3\% except for the two negative virtual atoms on the N=O bonds: +6\%). The maximal increase of non-H-atom valence population, 6\%, is observed for the C71 methyl atom. For the other atoms, $P_{\text{val}}$ increases from 2 to 3\% with $\kappa_{\text{hyd}} = 1.16$ compared to $\kappa_{\text{hyd}} = 1.10$. There is no clear tendency for the virtual-atom valence populations. The $P_{\text{val}}$ changes between corresponding models 2$a$ and 2$c$, 2$d$ and 2$f$, and 2$g$ and 2$i$ can be +6\% (C71) for real and +12\% for the virtual atoms, but reach 50\% (difference of 0.15 e) for those on the N=O bonds.

The dispersion of the differential angle between the theoretical one from \textit{CRYSTAL09} and from virtual-atom modelling is very small (from 14.6 to 15.4\,\textdegree, Table 3) and does not stand out from the MM\textsubscript{theo} results.

It is noteworthy that, in this modelling, all real atoms bear positive charges and all but two virtual atoms have a negative charge ($P_{\text{vir}} > 0$). This virtual-atom modelling seems very appropriate to extract dipole moments from theoretical structure factors. This can be easily understood because this model partitions the space with dipoles (+ on the atoms, − on the bonds). The optimal value of H-atom $\kappa$ is 1.13 to obtain the best moment, but one should keep in mind that the doubling of virtual atoms on the nitro N=O bonds is essential to achieve featureless residual maps, and simultaneously this causes a significant decrease of the molecular dipole moment.

### 3.3. Kappa model (KM\textsubscript{theo})

Six different models were tested for the KM\textsubscript{theo} modelling, with the following variable conditions (Table 4): (a) $\kappa_{\text{hyd}}$ constrained to 1.4, as suggested by Coppens (1997); or (b) $\kappa_{\text{hyd}}$ freely refined with 1.4 as a starting value; (c) different levels of equivalent-atom similarity restraints.
Table 3
Dipole moments from the virtual-atom refinements against theoretical structure-factor moduli.

<table>
<thead>
<tr>
<th>Model</th>
<th>Restraints/constraints</th>
<th>No. of variables</th>
<th>$RF$, $wR2F$ (%)</th>
<th>Goof</th>
<th>Dipole moment (D)</th>
<th>Angle between $\mu_{\text{theo}}$ and $\mu_{\text{calc}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>$\kappa_{\text{hyd}} = 1.1$</td>
<td>215</td>
<td>0.775</td>
<td>0.941</td>
<td>9.23</td>
<td>14.6</td>
</tr>
<tr>
<td>2b</td>
<td>$\kappa_{\text{hyd}} = 1.13$</td>
<td>215</td>
<td>0.764</td>
<td>0.927</td>
<td>10.74</td>
<td>14.7</td>
</tr>
<tr>
<td>2c</td>
<td>$\kappa_{\text{hyd}} = 1.16$</td>
<td>215</td>
<td>0.756</td>
<td>0.918</td>
<td>12.27</td>
<td>14.9</td>
</tr>
<tr>
<td>2d</td>
<td>$\kappa_{\text{hyd}} = 1.1$ chem. equiv. rest.†</td>
<td>215</td>
<td>0.774</td>
<td>0.941</td>
<td>9.28</td>
<td>15.2</td>
</tr>
<tr>
<td>2e</td>
<td>$\kappa_{\text{hyd}} = 1.13$ chem. equiv. rest.†</td>
<td>215</td>
<td>0.763</td>
<td>0.926</td>
<td>10.48</td>
<td>15.4</td>
</tr>
<tr>
<td>2f</td>
<td>$\kappa_{\text{hyd}} = 1.16$ chem. equiv. rest.†</td>
<td>215</td>
<td>0.756</td>
<td>0.917</td>
<td>11.97</td>
<td>15.4</td>
</tr>
<tr>
<td>2g</td>
<td>$\kappa_{\text{hyd}} = 1.1$ chem. equiv. cons.‡</td>
<td>205</td>
<td>0.770</td>
<td>0.939</td>
<td>9.36</td>
<td>15.1</td>
</tr>
<tr>
<td>2h</td>
<td>$\kappa_{\text{hyd}} = 1.13$ chem. equiv. cons.‡</td>
<td>205</td>
<td>0.767</td>
<td>0.928</td>
<td>10.42</td>
<td>15.2</td>
</tr>
<tr>
<td>2i</td>
<td>$\kappa_{\text{hyd}} = 1.16$ chem. equiv. cons.‡</td>
<td>205</td>
<td>0.759</td>
<td>0.918</td>
<td>11.90</td>
<td>15.3</td>
</tr>
</tbody>
</table>

† Chemical equivalence restraints on non-virtual atoms, with $\sigma = 0.01$ ($\kappa$ and valence populations of): C2 $\simeq$ C6; C3 $\simeq$ C5; O81 $\simeq$ O82; H2 $\simeq$ H6; H5 $\simeq$ H3; H71 $\simeq$ H72 $\simeq$ H73. ‡ Constrained atoms the same as in † with $\sigma = 0.0$.

Table 4
Results of the KM$_{\text{theo}}$ refinements.

No. of reflections = 15 074.

<table>
<thead>
<tr>
<th>Model</th>
<th>Restraints/ constraints</th>
<th>No. of variables</th>
<th>$\kappa_{\text{hyd}}$</th>
<th>$RF$, $wR2F$ (%)</th>
<th>Goof</th>
<th>Dipole moment (D)</th>
<th>Angle between $\mu_{\text{theo}}$ and $\mu_{\text{calc}}$ vectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>constraints†</td>
<td>38</td>
<td>1.4</td>
<td>1.950</td>
<td>0.329</td>
<td>11.25</td>
<td>13.8</td>
</tr>
<tr>
<td>3b</td>
<td>restraints†</td>
<td>45</td>
<td>1.4</td>
<td>1.953</td>
<td>0.329</td>
<td>11.28</td>
<td>13.5</td>
</tr>
<tr>
<td>3c</td>
<td>45</td>
<td>1.4</td>
<td>1.954</td>
<td>0.329</td>
<td>11.38</td>
<td>14.0</td>
<td></td>
</tr>
<tr>
<td>3d</td>
<td>constraints refined</td>
<td>42</td>
<td>2.766</td>
<td>0.329</td>
<td>8.78</td>
<td>16.0</td>
<td></td>
</tr>
<tr>
<td>3e</td>
<td>restraints refined</td>
<td>53</td>
<td>2.766</td>
<td>0.327</td>
<td>8.55</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>3f</td>
<td>refined</td>
<td>53</td>
<td>2.747</td>
<td>0.327</td>
<td>8.06</td>
<td>15.6</td>
<td></td>
</tr>
</tbody>
</table>

† Definition of chemical equivalency of atoms is the same as in VIR$_{\text{theo}}$ (see footnotes to Table 3).

The crystallographic agreement factors are much higher than in the two previous models because of the aspherical electron density which is not incorporated.

The dipole-moment magnitudes obtained are slightly higher than in the theoretical calculations for models with a constrained $\kappa_{\text{hyd}}$ value and drop when kappa is refined. The $\mu$ directions compared with the theoretical one are also closer for $\kappa_{\text{hyd}}$-constrained models (Table 4 and Fig. 8).

Restrictions imposed on $\kappa_{\text{hyd}}$ are crucial as they significantly influence the dipole-moment magnitudes, while the chemical-equivalence similarity constraints/restraints have almost no effect.

All $\kappa$ and $P_{\text{val}}$ values are collected in Table S5 in the supplementary material.

3.4. Conclusion – theoretical structure factors

Compared to a reference value of 10.6 D taken from a CRYSTAL09 computation, we were able to obtain a very good agreement in the modulus and direction of the dipole moment for the two MM and VIR models. The differential angle between the theoretical $\mu$ vector and vectors obtained in the calculations lies between 12.9 and 16.0°. Each group of sub-models requires specific constraints imposed on the $\kappa$ of H atoms. The constraints/restraints on the symmetry and chemical equivalency play a minor role. In addition, in the multipolar atom model, the choice of the order of multipolar expansion is a key issue. Over-parametrization must be avoided.

3.5. Experimental data refinements

3.5.1. Multipolar model (MM$_{\text{exp}}$). According to the theoretical calculations, to obtain a reliable $\mu$ value, the order of multipolar expansion should be fixed at a dipolar level for H atoms, an octupolar level for non-H atoms and hexadecapoles must be used for electron-rich bonds with cylindrical symmetry like C≡N. Together with the level of multipolar expansion, the treatment of ADPs of H atoms obtained from SHADE (constrained or restrained) was tested. The optimal constraints/restraints on symmetry and similarity on chemically equivalent atoms were kept in all refinements (for details see §2).

The summary for the MM$_{\text{exp}}$ calculations is presented in Table 5.
For all refinements, the residual Fourier electron density is spread over the unit cell with insignificant concentrations or depletions in the middle of the phenyl ring and close to the triple bond of the C=N group. As also seen by the crystallographic residual factors (2.3 < wR2F < 2.4%), these maps do not allow one to select the best refinement.

The analysis of the dipole-moment magnitudes and directions (Fig. 9) leads to the following conclusions:

(a) If we refer to the theoretical calculation, which means we trust the theoretical value and direction, the best dipole-moment vectors are obtained for models 4b–4c, with dipolar expansion of H atoms and ADPs constrained to SHADE values, no matter what the expansion of C=N is; the corresponding magnitudes are 11.7 and 11.1, respectively, close to the theoretical calculation.

(b) SHADE constraints imposed on the H-atom ADPs decrease the μ values for all models but 4a, with the largest drop observed for model 4c, which is the multipolar expansion predicted from theoretical calculations, to generate the μ value closest to the theoretical one (see above); in addition the SHADE ADP constraints increase the difference between the angles of the calculated and theoretical μ vectors.

(c) For the models with H-atom ADPs constrained, μdip, computed from the atomic dipole contribution only, is systematically larger than when H-atom ADPs are restrained.

(d) Refinement of significant hexadecapoles and quadrupoles in models 4a and 4d–4f has a minor influence.

It must be underlined that a small change of restraints imposed on H atoms results in significantly different values of the dipole moment (especially for softer restraints on the ADPs). However, the best model predicted from the theoretical calculations, with additional restraints on H-atom ADPs,

For all refinements, the residual Fourier electron density is spread over the unit cell with insignificant concentrations or depletions in the middle of the phenyl ring and close to the triple bond of the C=N group. As also seen by the crystallographic residual factors (2.3 < wR2F < 2.4%), these maps do not allow one to select the best refinement.

### Table 5

<table>
<thead>
<tr>
<th>Model</th>
<th>Multipolar level non-H/H atoms</th>
<th>No. of variables</th>
<th>RF, wR2F (%)</th>
<th>Goof</th>
<th>Total μ (monopoles/dipoles) (D)</th>
<th>μ total (monopoles/dipoles) (D) only for significant HEX/QUA</th>
<th>μ total (monopoles/dipoles) (D) with H-atom ADPs constrained to SHADE values</th>
<th>Angle between μ_theo and μ_calc vectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a</td>
<td>HEX/QUA</td>
<td>757</td>
<td>2.32</td>
<td>0.771</td>
<td>10.91 (12.91/2.65)</td>
<td>11.21 (12.95/2.76)</td>
<td>11.87 (14.62/3.21)</td>
<td>33.6/35.4†</td>
</tr>
<tr>
<td>4b</td>
<td>OCT/DIP</td>
<td>564</td>
<td>2.43</td>
<td>0.897</td>
<td>12.63 (13.50/0.96)</td>
<td>11.74 (13.42/1.73)</td>
<td>15.4/18.4</td>
<td>2.38</td>
</tr>
<tr>
<td>4c</td>
<td>OCT and HEX (C=N)/DIP</td>
<td>582</td>
<td>2.42</td>
<td>0.876</td>
<td>12.38 (13.15/1.64)</td>
<td>11.14 (12.82/2.10)</td>
<td>16.3/19.3</td>
<td>2.37</td>
</tr>
<tr>
<td>4d</td>
<td>HEX/DIP</td>
<td>717</td>
<td>2.36</td>
<td>0.784</td>
<td>9.44 (10.00/3.33)</td>
<td>9.48 (10.07/3.33)</td>
<td>8.95 (10.25/3.55)</td>
<td>11.8/12.2</td>
</tr>
<tr>
<td>4e</td>
<td>OCT/QUA</td>
<td>603</td>
<td>2.44</td>
<td>0.905</td>
<td>14.88 (16.15/1.50)</td>
<td>14.47 (15.73/1.53)</td>
<td>14.25 (16.31/2.19)</td>
<td>29.4/29.8</td>
</tr>
<tr>
<td>4f</td>
<td>OCT and HEX (C=N)/QUA</td>
<td>622</td>
<td>2.430</td>
<td>0.883</td>
<td>14.12 (15.63/1.71)</td>
<td>13.91 (15.41/1.64)</td>
<td>13.84 (16.15/2.41)</td>
<td>29.9/30.6</td>
</tr>
</tbody>
</table>

† SHADE restraints. ‡ SHADE constraints.

Figure 8


Figure 9

Dipole-moment vectors for the experimental multipolar models (grey, total; red, dipole moment using only atomic dipole contributions; blue, dipole moment using only atomic monopole charge contributions).
gives a $\mu$ value of 11.1 D, in excellent agreement with the theoretical 10.6 D value, but a slightly different direction.

### 3.5.2. Virtual-atom model (VIRexp)

Two groups of models were tested in this section: $5a$–$5d$ with one virtual atom on N=O bonds and $5e$–$5h$ with the two atoms, even if not deemed necessary. The virtual-atom refinement seems to work well to account for the aspherical electron density fitted to experimental data, as shown on the residual maps (Fig. 10). The corresponding static maps are encouraging despite the unique type of virtual-atom scattering factor used to describe all the covalent bonds. The strategy for dipole-moment predictions cannot be estimated from theoretical structure-factor refinement, according to the VIRtheo model (see §3.2), the optimal $\kappa_{\text{hyd}}$ for the correct magnitude and direction should be 1.13 and other constraints/restraints have no influence. This $\kappa_{\text{hyd}}$ value led to slightly lower ($5b$) or higher ($5f$) $\mu$ values than expected in the case of experimental data; therefore other values were tested. Moreover, the influence of ADP values from SHADE, which was crucial in MMexp refinements, was verified as well.

Eight different models with $\kappa_{\text{hyd}}$ constrained to 1.1, 1.13, 1.16 and 1.2, with different treatments of the H-atom ADPs and single or double virtual atoms on the N=O bonds were tested. The $\mu$ dependence on the H-atom ADPs is clearly visible especially for models $5a$–$5d$ (Table 6) with a difference of more than 5 D; the difference is lower for models $5e$–$5h$ (2 D). Refinement $5e$ ($\kappa = 1.1$) with H-atom ADPs constrained by SHADE gives the best dipole moment in both magnitude and direction (Fig. 11).

The comparison of $\mu_{\text{theo}}$ and $\mu_{\text{calc}}$ for the four models with different $\kappa_{\text{hyd}}$ constraints shows that the most affected parameters are the H-atom valence populations and the $\kappa$ and $P_{\text{vir}}$ of the virtual atoms positioned on the X−H bonds. A possible improvement would be to define a new scattering factor for C−H virtual atoms.

### 3.5.3. Kappa model (KMexp)

The best kappa model from the theoretical calculation predictions is with $\kappa_{\text{hyd}}$ restricted to the value 1.4, as recommended by Coppens et al. (1979). Refining the charge density with the geometry from the best multipolar model ($6a$, Table 7) results in slightly higher dipole-

---

**Table 6**

Results of the VIRexp refinement.

All results are given with an $I/\sigma(I) > 2$ cutoff for a reciprocal resolution up to $s = 1 \text{ \AA}^{-1}$. No. of reflections = 6164. The number of refined variables is 428. ModR: stereochemical restraints similar to VIRtheo, except for linearity ($\sigma_{l} = 0.01 \text{ \AA}$), similarity of kappa for the Lp’s of the nitro group are added. CER: chemical equivalence restraints are the same as in theoretical models and in MMexp.

<table>
<thead>
<tr>
<th>Model</th>
<th>Restraints</th>
<th>$RF_{w}$, wR2F (%)</th>
<th>Dipole moment $\mu$ (D)</th>
<th>$\mu$ with H-atom ADPs from SHADE not refined</th>
<th>Angle between $\mu_{\text{theo}}$ and $\mu_{\text{calc}}$ vectors</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>ModR $\kappa_{\text{hyd}} = 1.1$ CER</td>
<td>3.062, 1.22</td>
<td>9.02, 13.32</td>
<td>43.41/11.5†</td>
<td>9.02, 13.32, 43.41/11.5†</td>
</tr>
<tr>
<td>5b</td>
<td>ModR $\kappa_{\text{hyd}} = 1.13$ CER</td>
<td>3.064, 1.22</td>
<td>9.94, 15.14</td>
<td>31.7/11.1</td>
<td>31.7/11.1</td>
</tr>
<tr>
<td>5c</td>
<td>ModR $\kappa_{\text{hyd}} = 1.16$ CER</td>
<td>3.086, 1.22</td>
<td>11.24, 17.03</td>
<td>21.3/12.4</td>
<td>21.3/12.4</td>
</tr>
<tr>
<td>5d</td>
<td>ModR $\kappa_{\text{hyd}} = 1.2$ CER</td>
<td>3.094, 1.25</td>
<td>13.03, 19.05</td>
<td>21.1/12.8</td>
<td>21.1/12.8</td>
</tr>
<tr>
<td>5e</td>
<td>ModR $\kappa_{\text{hyd}} = 1.1$ CER</td>
<td>3.089, 1.25</td>
<td>10.70, 12.77</td>
<td>19.7/10.8</td>
<td>19.7/10.8</td>
</tr>
<tr>
<td>5f</td>
<td>ModR $\kappa_{\text{hyd}} = 1.13$ CER</td>
<td>3.094, 1.25</td>
<td>12.31, 14.79</td>
<td>15.7/11.4</td>
<td>15.7/11.4</td>
</tr>
<tr>
<td>5g</td>
<td>ModR $\kappa_{\text{hyd}} = 1.16$ CER</td>
<td>3.095, 1.25</td>
<td>13.78, 16.34</td>
<td>12.8/12.0</td>
<td>12.8/12.0</td>
</tr>
<tr>
<td>5h</td>
<td>ModR $\kappa_{\text{hyd}} = 1.2$ CER</td>
<td>3.101, 1.25</td>
<td>16.17, 18.64</td>
<td>10.8/14.1</td>
<td>10.8/14.1</td>
</tr>
</tbody>
</table>

† SHADE restraints. ‡ SHADE constraints.

---

Figure 10

Static deformation and Fourier residual maps for model 5f; contours ±0.05 e A^{-3}, resolution up to $s = 1 \text{ \AA}^{-1}$. 

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moment magnitude, but with a direction close to the expected one. In model 6b, no constraints were applied to $\kappa_{\text{hyd}}$ ($\kappa_{\text{hyd}} = 1.21$). In this case, the magnitude of $\mu$ is closer to the theoretical one, but its direction totally changes. The differences between the $\kappa$ and $P_{\text{val}}$ parameters of non-H atoms are negligible (except for C71 from the methyl group), whereas for H atoms the decrease of $\kappa$ (13–17%) in model 6b is related to an increase of $P_{\text{val}}$ (+18–23%; Fig. 12).

4. Conclusions

In this paper we have tried to achieve a thorough derivation of dipole moments from high-resolution X-ray diffraction refinement, as their estimation is by far the most difficult task, using theoretical and experimental structure factors.

Different electron-density models were tested (the kappa model, the multipolar model and the virtual-atom model) and it is shown that dipole moments (magnitude and direction) are extremely sensitive to the refinement strategy, in contrast to the topological analysis of the electron density: all models give the same topological properties (position, density and Laplacian at the critical point, bond paths...). The truthful refinement requires careful estimation of the H-atom positions and ADPs (neutron positions, anisotropy obtained by SHADE, no quadrupolar components) and leads to the right dipole moment in both multipole and virtual-atom models, but not in the kappa model.

Moreover, for the multipole electron-density modelling over-parametrization must be avoided as it can lead to wrong dipole populations because of an effective non-orthogonality of the restricted spherical harmonic basis set even if the least-squares residuals are slightly better. Therefore the H atoms should be refined up to dipoles, non-H atoms up to octupoles and non-H electron-rich atoms up to hexadecapoles, with the $\kappa$ and $\kappa'$ of H atoms restrained to 1.16 and 1.25, respectively.

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References


Table 7

Crystallographic statistics and dipole-moment moduli of the KM$_{\exp}$ refinement.

<table>
<thead>
<tr>
<th>Model</th>
<th>Restraints/</th>
<th>$\kappa_{\text{hyd}}$</th>
<th>No. of</th>
<th>$RF$,</th>
<th>Good $\mu$ (D)</th>
<th>Angle</th>
<th>Mean difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>constraints</td>
<td></td>
<td>variables</td>
<td>$wR^2F$</td>
<td>(%)</td>
<td>$\mu_{\text{theo}}$ and $\mu_{\text{calc}}$ vectors</td>
<td></td>
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<tr>
<td>6a</td>
<td>restraints†</td>
<td>1.4</td>
<td>42</td>
<td>4.454</td>
<td>2.830</td>
<td>13.76</td>
<td>23.8</td>
</tr>
<tr>
<td>6b</td>
<td>restraints refined (1.21)</td>
<td>50</td>
<td>4.447</td>
<td>2.815</td>
<td>8.90</td>
<td>91.9</td>
<td></td>
</tr>
</tbody>
</table>

† Restraints on chemical similarity are the same as in KM$_{\exp}$.
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