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Probing systematic errors in experimental charge density by multipole and invariom modeling: a twinned crystal of 1,10-phenanthroline hydrate

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Experimental and Computational details

Crystals of Phen ($C_{12}H_8N_2 \cdot H_2O$, M = 198.22) are trigonal, space group $P3_2$, at 100K: a = 17.5216(9), c = 8.4337(4) Å, V = 2242.31(19) $Å^3$, Z = 9 (Z' = 3), d_{calc} = 1.321 gcm^{-3}, μ(MoKα) = 0.87 cm^{-1}, F(000) = 936. Intensities of 177077 reflections were measured with a Bruker APEX2 CCD diffractometer [λ(MoKα) = 0.71072 Å, ω-scans, 2θ<100°], and 31284 independent reflections [R_{int} = 0.0317] were used in further refinement. These data were collected in three batches, a low-angle (2θ = −32°), a middle-angle (2θ = −62°), and a high-angle batch (2θ = −92°), in an omega-scan mode (Δω = 0.5°) with a detector to a sample distance of 4.1 cm at exposure times of 5 s for the low-angle reflections, 10 s for the middle-angle reflections, and 20 s for the high-angle reflections, respectively, to yield a high-resolution dataset (sinθ/λ up to 1.08 $Å^{-1}$). Raw data were integrated by using the program SAINT and then scaled, merged, and corrected for Lorentz-polarization effects using the package SADABS. Semi-empirical absorption correction from equivalents was applied using SADABS.

The observed systematic absences were consistent with space groups $P3_1$, $P3_2$, $P3_112$ and $P3_212$. The structure was solved in the space group $P3_2$ by direct methods and refined by the full-matrix least-squares technique against F^2 in the anisotropic approximation using SHELXTL PLUS 5.0 software.[1] Further inspection of the calculated and experimental structure factors revealed that many F_{exp}^2 were much greater than F_{calc}^2, suggesting the crystal studied was twinned, in line with data reported previously.[2] Note that among a series of probed crystals with a varying fraction of the second component, those having a higher BASF value were rejected on the spot; however, the best available crystal that was chosen for this study did not seem to suffer from twinning at the beginning. With twinning not considered, the refinement of the collected high-resolution dataset converged to wR2 = 0.1507 and GOF = 1.055 for all the independent reflections (R1 = 0.0526 was calculated against F for 25839 observed reflections with I>2σ(I)). The TwinRotMat routine of PLATON[3] applied to the dataset gave the twin law as (1 1 0, 0 -1 0, 0 0 -1), corresponding to merohedral twinning, with 31284 overlapping reflections. After the inclusion of this twin law (the twin component being 2.61%), the refinement converged to wR2 = 0.1363 and GOF = 0.957 for all the independent reflections (R1 = 0.0476 was calculated against F for 25841 observed reflections with I>2σ(I)). Besides lowering R factors (by 10%) and electron density residuals (by ~20%), the account for twinning led to somewhat decreased standard deviations in bond distances. Details of the data collection and refinement are

given in Table S1. CCDC 998980 and 998981 contain supplementary crystallographic data for Phen that can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

In both cases, the option LIST 2 was used in SHELXL to produce the files with filename extension 'fcf' containing F, which are corrected for twinning after the inclusion of the appropriate twin law; those were use as input files for the following multipole refinement. The two resulting datasets were modelled using the Hansen-Coppens formalism[4] as implemented in the program package XD;[5] input files were generated with the program MoleCoolQt.[6] For the invariom refinement, multipolar populations (up to hexadecapolar level) and kappa parameters from the invariom library[7] were assigned to all atoms, and then positional and displacement atomic parameters together with a scale factor were refined against all the experimental data ($2\theta = 100°$ or d = 0.463 Å) using statistical weights based on $1/\sigma(F_{obs})$. The invariom refinements were carried out against F and converged to R = 0.0410 and 0.0325, Rw = 0.0323 and 0.0215, GOF = 3.02 and 2.03 for 13478 and 13288 merged reflections with $I > 3\sigma(I)$ without an account for twinning and with it, respectively. The C-H and O-H bond distances were fixed at the values of 1.08225 and 0.96177 Å from the invariom database.[7]

For the conventional multipole refinements, the order of multipole expansion included octupoles for all non-hydrogen atoms and dipoles for hydrogens; those were adjusted against measured data using statistical weights based on $1/\sigma(F_{obs})$. The refinement of atomic coordinates and anisotropic displacement parameters (ADPs) was preformed against high-angle data ($\sin\theta/\lambda = 0.6 – 1.078$ Å^{-1}), and the refinement of all other parameters was performed up to $\sin\theta/\lambda = 1.078$ Å^{-1}. At the beginning, coordinates + ADPs were refined to obtained accurate positional coordinates and thermal parameters for all atoms, followed with the refinement of multipoles; both steps were repeated until R stopped decreasing. Then we introduced monopoles, first-order kappas and second-order kappas, all preceded and followed by coordinates + ADPs and multipoles refinement cycle, until repeating of any of these steps stopped leading to deviation from obtained parameters and/or decrease of R. The refinement was carried out against F and converged to R = 0.0402 and 0.0303, Rw = 0.0290 and 0.0189, GOF = 2.74 and 1.81 for 13478 and 13119 merged reflections with $I > 3\sigma(I)$ without an account for twinning and with it, respectively.

In all cases, the residual electron density maps were lacking significant features, with the lowest values observed for the refinement with an account for twinning (Table S1). The Hirshfeld test[8] yielded a highest difference in mean square displacement amplitudes along the bonds of $17 \cdot 10^{-4}$ Å^2 with twinning ignored and $11 \cdot 10^{-4}$ Å^2 (multipole model) or $7 \cdot 10^{-4}$ Å^2 (invariom model) with twinning taken into account. These values in all cases were random in character and indicated an overall satisfactory deconvolution of thermal motion and electron density being better after the twinning was taken into account or the invariom approximation was introduced.

Topological analysis of the resulting functions $\rho(\mathbf{r})$ was carried out using the WINXPRO program package.[9] Potential energy density $v(\mathbf{r})$ was evaluated through the Kirzhnits's

approximation[10] for kinetic energy density function g(**r**). Accordingly, the g(**r**) function is described as $(3/10)(3\pi^2)^{2/3}[\rho(\mathbf{r})]^{5/3}+(1/72)|\nabla\rho(\mathbf{r})|^2/\rho(\mathbf{r})+1/6\nabla^2\rho(\mathbf{r})$, giving in conjunction with the virial theorem $(2g(\mathbf{r})+v(\mathbf{r})=1/4\nabla^2\rho(\mathbf{r}))$[11] the expression for v(**r**). The interaction energies were estimated by means of the Espinosa's correlation scheme – a semiquantitative relation between the energy of an interaction and the value of the potential energy density function v(**r**) in its *bcp*.[12, 13] Having a very simple form as 0.5v(**r**), it was repeatedly shown to give accurate estimates in many cases (those are succinctly summarized in [14]). The interaction energies thus obtained were shown to accurately reproduce the energy of a crystal lattice[15-18]; the discrepancy between the crystal lattice energies estimated in such a manner from X-ray diffraction data and those measured experimentally can be as small as 0.2 kcal/mol[15, 19]. The latter value, divided by a number of interactions used to obtain the sublimation enthalpy by this approach, may be thought of as uncertainty in the interaction energies estimated by Espinosa's correlation thus being of ~0.02 kcal/mol.

Note that both using H-ADPs estimated with the SHADE server[20] and including higher multipoles from the invariom database for H atoms[21, 22] gave virtually identical results; the energy of intermolecular interactions varied within 0.02 kcal/mol only.

Table S1. Details of data collection and of spherical, multipole and invariom refinements against experimental structure factors for Phen**.**

Compound	$C_{12}H_8N_2 \cdot H_2O$
M	198.22
T	100K
Space group	$P3_2$
Crystal system	Trigonal
a, Å	17.5216(9)
c, Å	8.4337(4)
γ,°	120.00
V, $Å^3$	2242.31(19)
Z	9
Density, gcm^{-3}	1.321
F(000)	936
μ (MoK_α), cm^{-1}	0.87
Crystal size, mm	0.25 x 0.25 x 0.25
Scan technique	ω-scan with 0.5° step in ω

Absorption correction (MoKα)	semiempirical from equivalents
θ_{max}, °	50.0
Number of measured refl.	177077
Number of independent refl. (R_{int})	31284 (0.0317)
Number of observed refl. with I>2σ(I)	25841

	No account for twinning	With account for twinning
	Spherical refinement	
Volumetric content of individuals	-	97:3
wR2	0.1507	0.1363
R1 calculated against F	0.0526	0.0476
GOF	1.055	0.957
ρ_{max}/ρ_{min}, eÅ^{-3}	0.587/-0.446	0.571/-0.405
	Multipole refinement	
Number of rfln. with I>3σ(I)	13478	13119
R1 calculated against F	0.0402	0.0303
Rw calculated against F	0.0290	0.0189
GOF	2.74	1.81
ρ_{max}/ρ_{min}, eÅ^{-3}	0.192/-0.244	0.128/-0.145
	Invariom refinement	
Number of rfln. with I>3σ(I)	13478	13288
R1 calculated against F	0.0410	0.0325
Rw calculated against F	0.0323	0.0215
GOF	3.02	2.03
ρ_{max}/ρ_{min}, eÅ^{-3}	0.186/-0.210	0.125/-0.165

Single point PW-DFT calculations of the atomic configuration for Phen obtained from original X-ray diffraction data (although the positions of all non-hydrogen atoms changed only slightly after the twinning was taken into account) were performed with periodic boundary conditions using VASP 5.3.3 program.[23-26] To build the electron density with the highest accuracy available, a plane wave expansion (which does not suffer from a superposition error in contrast to gaussian basis sets) was applied with a kinetic energy cutoff of 1360 eV, and projected augmented wave (PAW) potentials were used with the smallest core radii.[27] All calculations were performed within the generalized gradient approximation (exchange–correlation functional PBE).[28, 29] The resulting electron density

function was obtained as a three dimensional dataset containing 480 × 480 × 240 points; those were sufficient to localize all the critical points for expected chemical and hydrogen bonds. The topological analysis of the calculated electron density function was carried out using an AIM program[30] included in the ABINIT program package. To evaluate atomic charges within the "Atoms in Molecules" theory,[11] a Yu-Trinkle method[31] was used as implemented in the CRITIC2 program.[32]

Supplementary references

1. G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.
2. Y.-P. Tian, C.-Y. Duan, X.-X. Xu and X.-Z. You, *Acta Cryst. C*, 1995, **51**, 2309-2312.
3. A. L. Spek, Utrecht University, Utrecht, 2001.
4. N. K. Hansen and P. Coppens, *Acta Crystallogr. A*, 1978, **34**, 909-921.
5. A. Volkov, P. Macchi, L. J. Farrugia, C. Gatti, P. Mallinson, T. Richter and T. Koritsanszky, 2006.
6. C. B. Hubschle and B. Dittrich, *J. Appl. Cryst.*, 2011, **44**, 238-240.
7. B. Dittrich, C. B. Hubschle, K. Propper, F. Dietrich, T. Stolper and J. J. Holstein, *Acta Cryst. B*, 2013, **69**, 91-104.
8. F. L. Hirshfeld, *Acta Crystallogr. A*, 1976, **32**, 239-244.
9. A. Stash and V. Tsirelson, *J. Appl. Crystallogr.*, 2002, **35**, 371-373.
10. D. A. Kirzhnits, *Sov. Phys. JETP*, 1957, **5**, 64-72.
11. R. F. W. Bader, *Atoms In molecules. A Quantum Theory*, Clarendron Press, Oxford, 1990.
12. E. Espinosa, E. Molins and C. Lecomte, *Chem. Phys. Letts.*, 1998, **285**, 170-173.
13. E. Espinosa, I. Alkorta, I. Rozas, J. Elguero and E. Molins, *Chem. Phys. Letts.*, 2001, **336**, 457-461.
14. K. A. Lyssenko, *Mendeleev Commun.*, 2012, **22**, 1-7.
15. K. A. Lyssenko, A. A. Korlyukov and M. Y. Antipin, *Mendeleev Commun.*, 2005, 90-92.
16. Y. V. Nelyubina and K. A. Lyssenko, *Chem. Eur. J.*, 2012, **18**, 12633-12636.
17. K. A. Lyssenko, A. A. Korlyukov, D. G. Golovanov, S. Y. Ketkov and M. Y. Antipin, *J. Phys. Chem. A*, 2006, **110**, 6545-6551.
18. I. V. Glukhov, K. A. Lyssenko, A. A. Korlyukov and M. Y. Antipin, *Faraday Discuss.*, 2007, **135**, 203-215.
19. Y. V. Nelyubina, I. V. Glukhov, M. Y. Antipin and K. A. Lyssenko, *Chem. Comm.*, 2010, **46**, 3469-3471.
20. A. O. Madsen, *J. Appl. Crystallogr.*, 2006, **39**, 757-758.
21. B. Dittrich, C. B. Hubschle, J. J. Holstein and F. P. A. Fabbiani, *J. Appl. Cryst.*, 2009, **42**, 1110-1121.
22. B. Dittrich and M. A. Spackman, *Acta Cryst. A*, 2007, **63**, 426-436.
23. G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, **47**, 558.
24. G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251.
25. G. Kresse and J. Furthmüller, *Comput. Mat. Sci.*, 1996, **6**, 15.
26. G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169.
27. G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758.
28. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
29. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.
30. X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, P. Ghosez, J.-Y. Raty and D. C. Allan, *Comput. Mat. Sci.*, 2002, **25**, 478–492.
31. M. Yu and D. R. Trinkle, *J. Chem. Phys.*, 2011, **134**, 064111.
32. A. Otero-de-la-Roza, E. R. Johnson and V. Luaña, *Comp. Phys. Comm.*, 2014, **185**, 1007–1018.

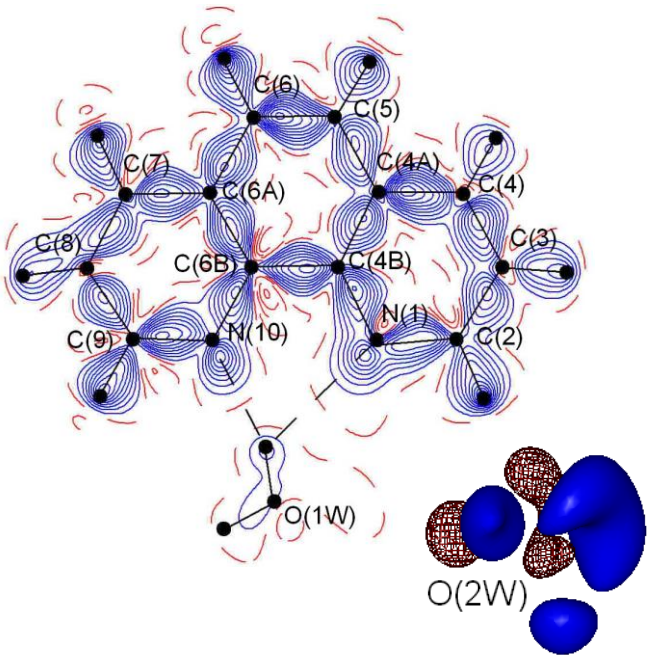
Supplementary Table S2. Interatomic distances and topological parameters of ρ(**r**) distributions in bcps for H-bonds in crystalline Phen based on multipole and invariom (in parentheses) modeling of X-ray diffraction data without an account for twinning and (first entry) and with it (second entry). The third entry (given in italics) denotes the values obtained from periodic quantum chemical calculations with original X-ray diffraction data used as a starting model.

Interaction	d, Å [a)]	ρ(**r**), eÅ^{-3}	$\nabla^2\rho$(**r**), eÅ^{-5}	-v(**r**), a.u.	h_e(**r**), a.u.	E_{int}, kcal/mol
O(1W)…H(1WB)	2.9359(11) 2.9358(13) *2.9359*	0.18 (0.14) 0.15 (0.14) *0.14*	2.74 (1.83) 2.68 (1.82) *1.59*	0.0235 (0.0151) 0.0195 (0.0150) *0.0148*	0.0025 (0.0016) 0.0042 (0.0020) *0.0016*	7.4 (4.7) 6.1 (4.7) *4.6*
O(2W)…H(2WB)	2.9649(10) 2.9648(11) *2.9649*	0.02 (0.13) 0.06 (0.13) *0.14*	0.92 (1.75) 2.64 (1.75) *1.59*	0.0034 (0.0142) 0.0111 (0.0142) *0.052*	0.0031 (0.0020) 0.0082 (0.0020) *0.0014*	1.1 (4.5) 3.8 (4.4) *4.8*
O(3W)…H(3WB)	2.9374(9) 2.9376(10) *2.9374*	0.15 (0.14) 0.06 (0.14) *0.15*	2.99 (1.75) 2.43 (1.75) *1.68*	0.0200 (0.0142) 0.0128 (0.0142) *0.0178*	0.0055 (0.0020) 0.0082 (0.0020) *0.0011*	6.3 (4.7) 4.0 (4.7) *5.2*
N(10)…H(1WA)	2.9171(10) 2.9182(13) *2.9171*	0.20 (0.15) 0.07 (0.15) *0.19*	2.74 (1.91) 2.45 (1.91) *1.48*	0.0257 (0.0171) 0.0112 (0.0171) *0.0208*	0.0014 (0.0014) 0.0072 (0.0014) *0.0021*	8.1 (5.4) 3.5 (5.4) *6.5*
N(1)…H(1WA)	3.2124(11) 3.2127(13) *3.2124*	0.06 (0.06) 0.05 (0.06) *0.06*	0.91 (0.71) 0.78 (0.72) *0.73*	0.0054 (0.0047) 0.0041 (0.0048) *0.0046*	0.0021 (0.0013) 0.0020 (0.0013) *0.0015*	1.7 (1.5) 1.3 (1.5) *1.4*
N(10')…H(2WA)	2.9660(10) 2.9663(12) *2.9660*	0.07 (0.14) 0.09 (0.14) *0.17*	1.84 (1.73) 2.43 (1.74) *1.41*	0.0089 (0.0149) 0.0128 (0.0149)	0.0051 (0.0015) 0.0062 (0.0015)	2.8 (4.7) 4.0 (4.7) *5.4*

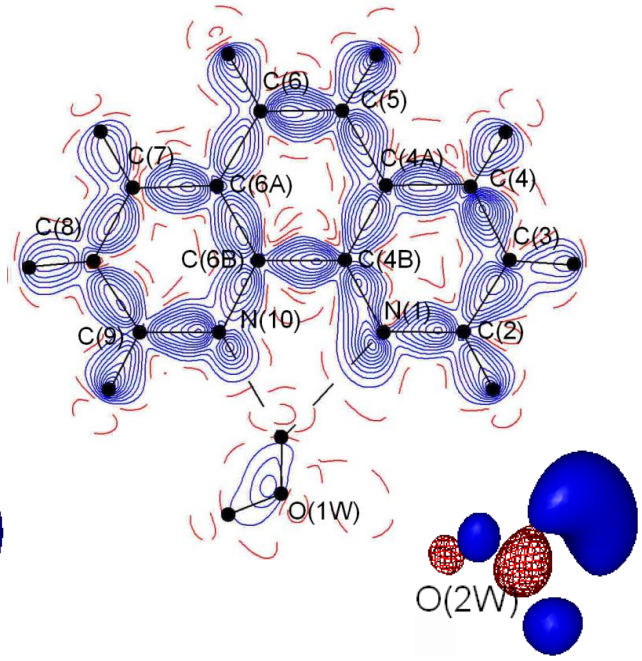
				0.0173	*0.0007*	
N(1')…H(2WA)	3.1669(10) 3.1647(12) *3.1669*	0.04 (0.07) 0.05 (0.07) *0.07*	0.81 (0.80) 0.91 (0.79) *0.79*	0.0041 (0.0054) 0.0047 (0.0053) *0.0061*	0.0022 (0.0015) 0.0024 (0.0015) *0.0014*	1.3 (1.7) 1.5 (1.7) *1.9*
N(10")…H(3WA)	2.9181(12) 2.9188(13) *2.9181*	0.09 (0.16) 0.09 (0.16) *0.19*	2.44 (1.95) 2.40 (1.95) *1.48*	0.0130 (0.0175) 0.0125 (0.0175) *0.0202*	0.0062 (0.0014) 0.0062 (0.0014) *0.0018*	4.1 (5.5) 4.0 (5.5) *6.3*
N(1")…H(3WA)	3.1832(9) 3.1834(11) *3.1832*	0.05 (0.06) 0.04 (0.06) *0.07*	0.90 (0.72) 0.88 (0.73) *0.76*	0.0047 (0.0048) 0.0045 (0.0049) *0.0057*	0.0023 (0.0014) 0.0023 (0.0014) *0.0015*	1.5 (1.5) 1.4 (1.5) *1.8*

[a)] d stands for the distance between a donor and an acceptor of proton.

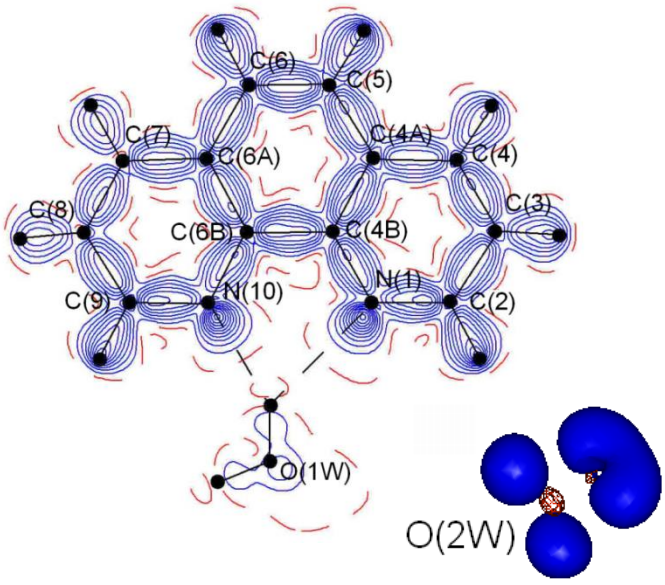
Supplementary Figure S1. DED distributions for phenanthroline and water molecules obtained by multipole refinement without an account for twinning (**A**) and with it (**B**) and by invariom refinement (**C**), which in both cases gave fully identical results, against X-ray diffraction data. In 2D representation, contours are drawn through 0.1 eÅ^{-3}, the negative contours are dashed; in 3D representation, isosurfaces of DED = 0.4 eÅ^{-3} are shown by blue, those with DED = –0.35 eÅ^{-3} by red wireframe.



A



B



C

Supplementary Figure S2. Interaction energies in kcal/mol from top to bottom for hygrogen bonds O-H…O beetween water molecules, for stronger component of O-H...N bonds and for their weaker component plotted against donor-acceptor distance (Å). Mult_twin or Inv_twin and Mult_notwin or Inv_notwin stand for multipole or invariom refinement with and without an account for twinning, respectively; Quant stands for periodic quantum chemistry.