

Communication

Effects of Empirical Dispersion Energy on the Geometrical Parameters and Relative Energy of a Salicylideneaniline Molecular Switch in the Solid State

Jean Quertinmont ¹, Tom Leyssens ², Johan Wouters ¹ and Benoît Champagne ^{1,*}

¹ Unité de Chimie Physique Théorique et Structurale, Namur Institute of Structured Matter, University of Namur, 61 Rue de Bruxelles, B-5000 Namur, Belgium.

² Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, 1 Place Louis Pasteur, B-1348 Louvain-La-Neuve, Belgium.

* Correspondence: benoit.champagne@unamur.be; Tel.: +32-81-724554

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Abstract: A single paragraph of about 200 words maximum. For research articles, abstracts should give a pertinent overview of the work. We strongly encourage authors to use the following style of structured abstracts, but without headings: 1) Background: Place the question addressed in a broad context and highlight the purpose of the study; 2) Methods: Describe briefly the main methods or treatments applied; 3) Results: Summarize the article's main findings; and 4) Conclusion: Indicate the main conclusions or interpretations. The abstract should be an objective representation of the article, it must not contain results which are not presented and substantiated in the main text and should not exaggerate the main conclusions. [to be done]

Keywords: salicylideneaniline molecular crystals, solid state geometry optimizations, dispersion energy corrections.

1. Introduction

Thermochromic and photochromic compounds have been extensively studied and still attract a lot of attention as they have many potential applications [1–8]. With the focus moving from the liquid phase to the more practical solid one, computational methods well set for quantum calculations of inorganic solids are now being challenged by the molecular crystalline state. In particular, accurate description of the intramolecular parameters (defined by the fractional coordinates of the asymmetric unit) and the intermolecular ones (defined by the unit cell parameters) is required as a starting point for the prediction and study of their properties. Density functional theory (DFT) was recently shown to be an efficient tool granted that the appropriate exchange-correlation functional (XCF) is used [9,10]. In Ref 9, Ruggiero and co-workers have assessed the reliability of a range of XCFs for the optimization of three pyridine carboxylic acid crystals and they have highlighted the performances of ω B97X [11]. Then in Ref 10, we have shown the effectiveness of three XCFs (HSEsol [12], PBEsol0, and ω B97X [11]) to optimize the molecular and crystal structures of three salicylideneanilines. Still, with respect to the XCFs used so far, for a precise description of the solid state, modifications can be made to DFT by adding London dispersion interactions to the DFT energy (Equation 1) in the form of empirical terms as proposed by Grimme [13].

$$E_{\text{DFT-D}} = E_{\text{DFT}} + E_{\text{disp}}, \quad (1)$$

where E_{disp} is the empirical dispersion energy. Here we consider the second iteration of that scheme, containing less empirical parameters than the first one, and known as DFT-D2. General expressions for E_{disp} reads:

$$E_{\text{disp}} = -s_6 \sum_{\mathbf{g}} \sum'_{ij} f_{\text{dmp}}(R_{ij,\mathbf{g}}) \frac{C_6^{ij}}{R_{ij,\mathbf{g}}^6}, \quad (2)$$

with the first summation running over all lattice vectors, $\mathbf{g}$, and the second one running over all atom pairs (excluding the self-interaction case, when $i=j$ for $\mathbf{g}=0$), s_6 is a scaling factor depending on the functional, $C_6^{ij} = \sqrt{C_6^{ii} C_6^{jj}}$ is the dispersion coefficient for the ij pair, $R_{ij,\mathbf{g}}$ is the distance between the atom i in the reference cell ($\mathbf{g}=0$) and the atom j in the cell $\mathbf{g}$, and $f_{\text{dmp}}(R_{ij,\mathbf{g}})$ is a damping function:

$$f_{\text{dmp}}(R_{ij,\mathbf{g}}) = \left[1 + e^{-d \left(\frac{R_{ij,\mathbf{g}}}{R_{\text{vdw}}} - 1 \right)} \right]^{-1} \quad (3)$$

In the latter expression, R_{vdw} is the sum of the van der Waals radii of the i and j atoms and d defines the steepness of the function. Since this scheme was parameterized for clusters, Ugliengo and coworkers proposed to scale the coefficients published by Grimme in order to better describe the dispersion energy in molecular crystals, leading to DFT-D* (these modifications include a decrease of the scaling factor by a factor 0.95 and a scale up of the atomic van der Waals radii by 1.05 and 1.30 for heavy and hydrogen atoms, respectively) [14]. This modification results in smaller dispersion energies.

In this Paper, we aim at evaluating the effects of adding these empirical dispersion energy terms (DFT-D and DFT-D*) on the optimized geometrical parameters of a molecular crystal from the salicylideneanilines family, (E)-2-methoxy-6-(pyridine-3-yliminomethyl)phenol (PYV3, Figure 1). This compound is in fact a molecular switch that can commute between an enol (E) and a keto (K) form, so that our second focus is on the relative energies between these two forms. These theoretical predictions performed with DFT-D and DFT-D* XCFs are compared to X-ray diffraction (XRD) data as well as to those predictions obtained with more traditional DFT functionals [10]. The Paper is organized as follows: next Section summarizes the key computational aspects (additional details can be found in Ref. 10); Section 3 presents and discusses the results before conclusions are drawn in Section IV.

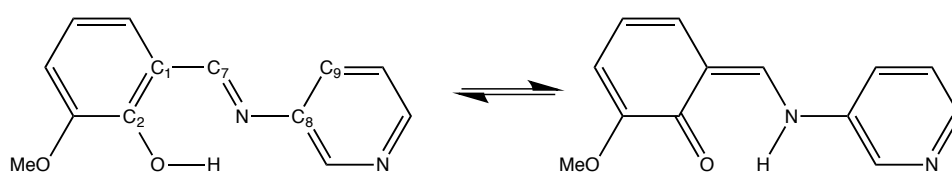


Figure 1. Structure and keto-enol equilibrium of the studied salicylideneaniline: (E)-2-methoxy-6-(pyridine-3-yliminomethyl)phenol (PYV3). Key bonds and atoms for characterizing the geometries are highlighted on the enol structure.

2. Computational aspects

Calculations were performed with the Crystal14 package [15] using various XCFs: B3LYP [16], PBE [17], PBE0 [18], PBEsol [19], PBEsol0, and ω B97X [11] with and without including London dispersion interactions. This is achieved by using the empirical dispersion corrections due to Grimme [13]. First, the original parameters were employed (DFT-D), then those revised for the crystalline state (DFT-D*) [14]. The steepness d of the damping function was set to 20 and a cutoff distance of 25 Å was set for the lattice summations. The default integration grid was used; the truncation criteria for the bielectronic integrals (TOLINTEG keyword) were set to 8 8 8 16 for all XCFs, except for ω B97X: 7 7 7 7 16; the maximum order of the shell multipole is kept to the default, as well as all convergence

criteria for both the SCF cycles and the optimization. A Pack–Monkhorst shrinking factor of 6 was used, yielding 64 integration points in the irreducible Brillouin zone. Pople’s 6-31G(d,p) basis set was used as taken from Basis Set Exchange [19,20].

3. Results and discussion

3.A. Crystal structures and molecular geometries

First the optimized structures of PYV3 obtained using the three “levels” of DFT, *i.e.* DFT, DFT-D, and DFT-D*, and a selection of XCFs are compared to X-Ray Diffraction (XRD) data [21]. The focus is set first on the unit cell volumes (Table 1) and the unit cell parameters (Figures 2, then on key bond lengths and angles (Figures 3 and 4).

On the unit cell volume, using the reference DFT XCFs yields either large errors with respect to XRD data (B3LYP 17%, PBE 12%, and PBE0 11%) or volumes within a satisfying range ($\leq 2\%$): PBEsol < -1%, PBEsol0 < -1%, ω B97X -2%. Then, the addition of empirical dispersion energy leads overall to smaller unit cell volumes. In the case of DFT-D, the unit cells are over-contracted, meaning relative errors ranging from -15 to -8%, while the DFT-D* results tone down this effect to provide volumes either in closer agreement with the experimental values for those XCFs performing poorly with DFT (B3LYP -5%, PBE -3%, and PBE0 -6%), or still over-contracting the unit cell volume for PBEsol, PBEsol0, and ω B97X (errors between -11.6 and -11.2%).

Table 1. Differences of unit cell volume [$\Delta V = V(E) - V(\text{XRD})$, in $\text{\AA}^3$, and $\Delta V/V = \Delta V/V(\text{XRD})$, in %] as calculated with different XCFs and models for PYV3. The 6-31G(d,p) basis set was applied for all calculations.

Method	DFT	DFT-D	DFT-D*
B3LYP	189.0 (17.2%)	-112.9 (-10.3%)	-52.3 (-4.8%)
PBE	129.4 (11.8%)	-89.3 (-8.1%)	-36.2 (-3.3%)
PBE0	117.3 (10.7%)	-112.3 (-10.5%)	-61.1 (-5.6%)
PBEsol	-5.2 (-0.5%)	-169.3 (-15.4%)	-122.9 (-11.2%)
PBEsol0	-7.0 (-0.6%)	-170.5 (-15.5%)	-127.2 (-11.6%)
ω B97X ¹	-21.9 (-2.0%)	-163.4 (-14.9%)	-124.9 (-11.4%)

¹ TOLINTEG = 7 7 7 7 16

Figure 2 shows the unit cell parameters (*a*, *b*, and *c*) variations with respect to XRD data. When using conventional DFT XCFs (B3LYP, PBE, and PBE0) variations on the unit cell parameters, Figure 2.a, all are positive (except for PBE) and larger than 3%. On the other hand, when using XCFs optimized for the solid state (PBEsol and PBEsol0) as well as ω B97X the differences with respect to XRD data are smaller than 3% and not systematically positive (leading to error cancellation on the estimated unit cell volume, *e.g.* for PBEsol: the error on *a*, -2.7%, is partially cancelled by the one of *b*, 1.9%, while *c* is fairly accurate, 0.5%).

In the case of DFT-D*, Figure 2.b, the *a* parameter is strongly underestimated (errors between -6 and -10%) for all XCFs while the errors on *b* are positive (except for ω B97X) allowing for error compensations on the volume when *c* is accurate (between -0.8 and 0.4%): B3LYP, PBE, and PBE0. This explains why the volume is closer to experiment with these three functionals (-5.6 to -3.3%) than with PBEsol, PBEsol0, and ω B97X (-11.6 to -11.2%). Indeed, for the latter XCFs, the errors on the *a* and *c* parameters are both negative (-2.3 to -3.1%) and are not compensated by the errors on *b*. Finally, the DFT-D model, Figure 2.c, results in strong and systematic underestimations of all parameters, ranging from -2.5 to -7.7%. A distinction can be made for the *a* parameter as determined with B3LYP, PBE, and PBE0 for which the error is smaller, ~3%, than with the other XCFs, ~7%, while the errors for *b* and *c* are similar among the XCFs. This results in B3LYP, PBE, and PBE0 volumes that are slightly better than the PBEsol, PBEsol0, and ω B97X ones.

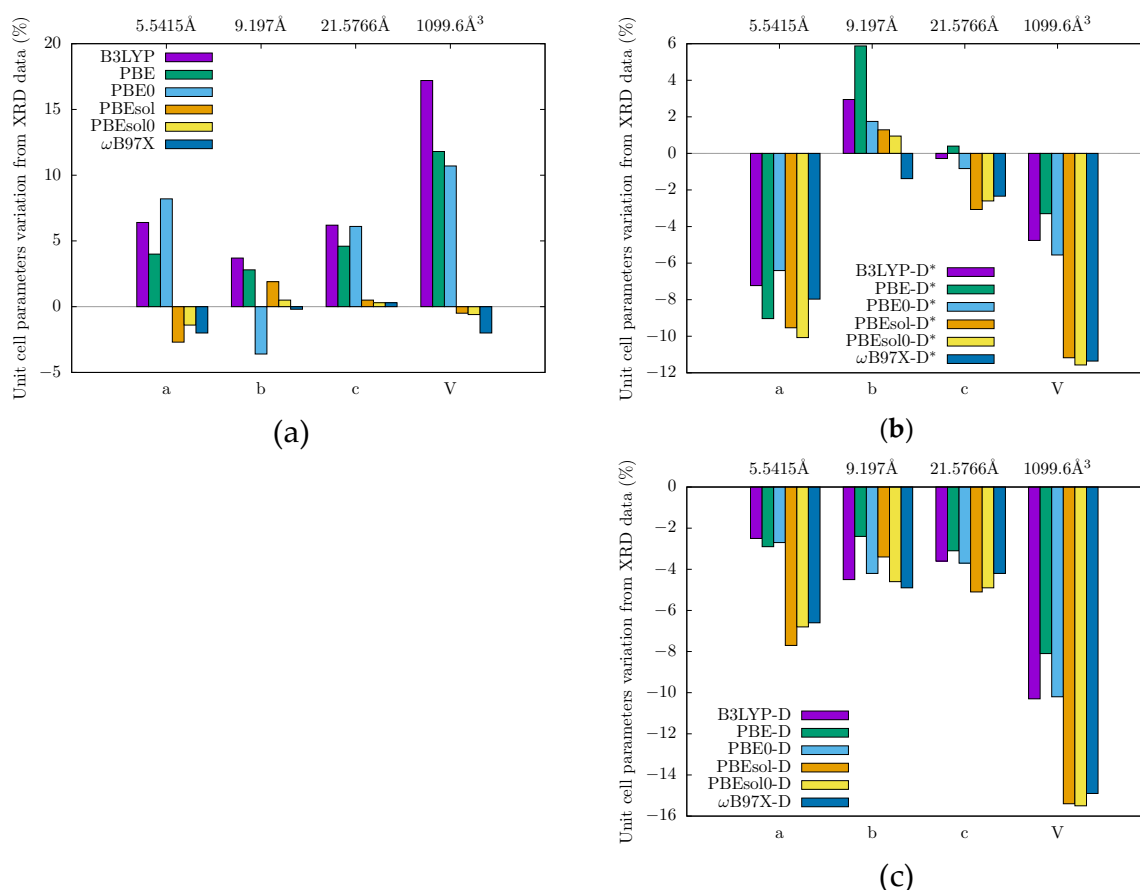


Figure 2. Differences (in %) between the optimized unit cell parameters and the XRD values as a function of the XCF, $\Delta = [X(\text{Calc.}) - X(\text{XRD})]/X(\text{XRD})$: (a) with DFT; (b) with DFT-D*; (c) with DFT-D. The XRD values are given on the top of each figure. The 6-31G(d,p) basis set was employed for all calculations.

Accurate unit cell parameters constitute a good starting point for further investigations of thermodynamical or optical properties, at least, as long as the bond lengths and angles are also accurately modelled. Figure 3 shows the variations with respect to XRD data for key bond lengths along the O-C₂-C₁-C₇-N-C₈ path (Figure 1). Moreover, two bond length ratios are considered, the N- and C-ratios, which describe the π -conjugation and are defined as follow:

$$\text{N-ratio} = d(\text{C}_1\text{-C}_7)/d(\text{C}_2=\text{C}_1), \quad (3)$$

$$\text{C-ratio} = d(\text{N-C}_8)/d(\text{C}_7=\text{N}), \quad (4)$$

The comparison to experiment is not presented for DFT-D since we have shown above its poor reliability for the unit cell parameters. Figures 3a, for DFT, and 3b, for DFT-D*, highlight the systematic underestimation (overestimation) of the single (double) bond lengths, with the exception of C₁-C₇ and C₇=N with ωB97X. Still, in the worst cases, these errors are smaller than 0.025 Å and generally of the order of 0.01 Å. This results in slightly too small N-/C-ratios, especially in the case of the two GGA XCFs, PBE and PBEsol, whereas the ωB97X's ratios are slightly positive. The DFT-D* results are extremely similar to the DFT ones since the differences do not exceed 3 mÅ. This affects the ratios by about the same amount.

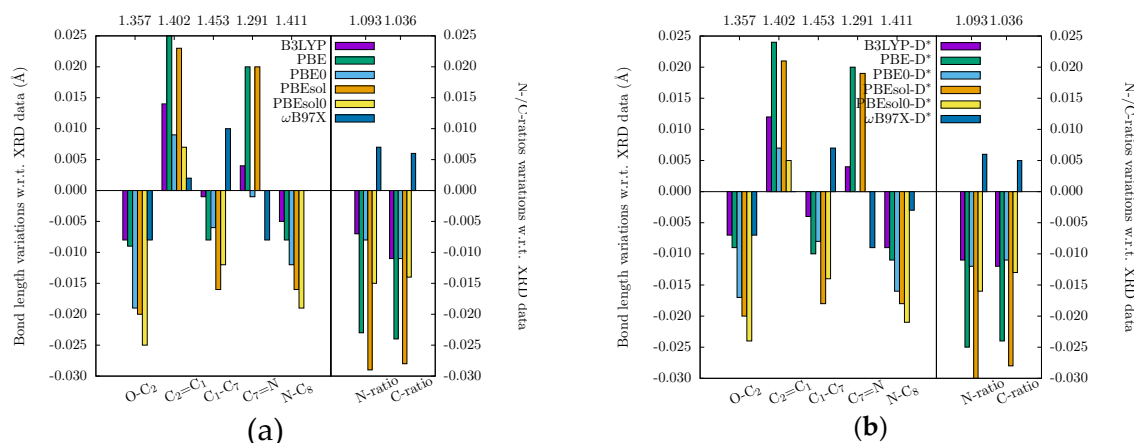


Figure 3. Differences between the bond lengths of the optimized structure and of the XRD data as a function of the XCF, $\Delta = [d(\text{DFT}) - d(\text{XRD})]$: (a) with DFT; (b) with DFT-D*. The XRD values are given on the top of each figure. The 6-31G(d,p) basis set was employed for all calculations.

As for the valence and torsion angles, the variations with respect to XRD data are presented in Figure 4 for two valence angles ($\text{C}_1\text{-C}_7\text{-N}$ and $\text{C}_7\text{-N-C}_8$), the three torsion angles involving the $\text{C}_7\text{=N}$ bond ($\text{C}_2\text{-C}_1\text{-C}_7\text{-N}$, $\text{C}_1\text{-C}_7\text{-N-C}_8$, and $\text{C}_7\text{-N-C}_8\text{-C}_9$), one torsion angle associated with the H-bond ($\text{C}_2\text{-O-N-C}_7$), and one torsion angle describing the global torsion of the molecule ($\text{C}_2\text{-C}_1\text{-C}_8\text{-C}_9$). Like previously, only DFT and DFT-D* results are discussed (Figure 4a and 4b, respectively). The absolute errors on the valence angles are within the $[-2^\circ; 2^\circ]$ range for all XCFs and both types of DFT levels ($\sim 2\%$ of relative error). Then, for the torsion angles, in the case of DFT without dispersion, they are systematically underestimated, except for ωB97X . Furthermore, the error on the molecular torsion (angle $\text{C}_2\text{-C}_1\text{-C}_8\text{-C}_9$) and, to a smaller extent on the angle $\text{C}_7\text{-N-C}_8\text{-C}_9$, is quite large for those XCFs that poorly perform for the unit cell parameters (with errors ranging between -5.7° and -10.5° for B3LYP, PBE, and PBE0) whereas for the other XCFs (PBEsol, PBEsol0, and ωB97X), the deviations are much small: -3.1° , -3.1° , and -1.0° , respectively. This highlights the key role of the torsion angles on the unit cell parameters or, in other words, their interdependence. It is however difficult to tell which one is the driving force and creates a bias on the other quantity.

When using the DFT-D* model, the amplitude of the errors is greatly reduced compared to standard DFT, in particular for B3LYP, PBE, and PBE0. Note that the scale of Figure 4a for DFT goes from -12 to 4° while that of Figure 4b for DFT-D*, from -2 to 4° . For DFT-D*, the errors on the torsion angles are mainly positive, except for the $\text{C}_1\text{-C}_7\text{-N-C}_8$ angle. For the important molecular torsion ($\text{C}_2\text{-C}_1\text{-C}_8\text{-C}_9$), the error is around 1° for all XCFs, except for PBE0 ($< 1^\circ$) and ωB97X (2°), which is on par with the errors of PBEsol, PBEsol0, and ωB97X with DFT for the same angle. Accurate molecular torsions are obtained in parallel with accurate unit cell parameters but the molecular torsion is not the only criterion to satisfy.

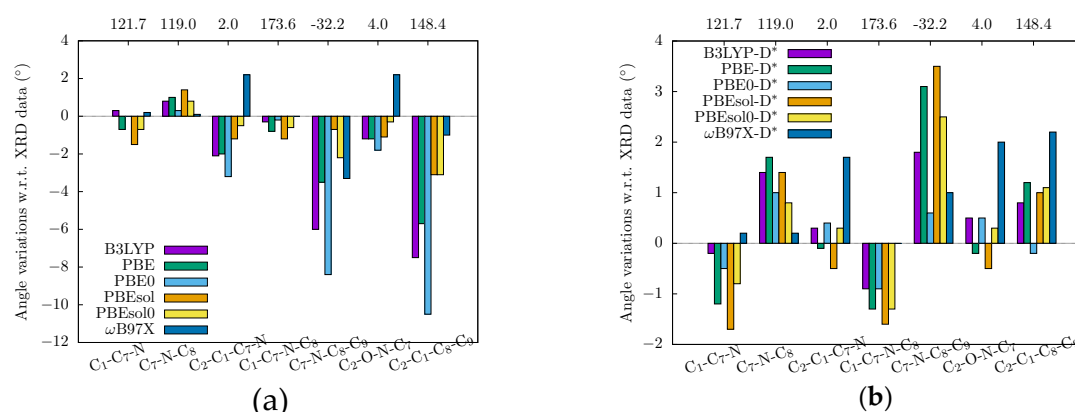


Figure 4. Differences between the angles of the optimized structure and of the XRD data as a function of the XCF, $\Delta = [a(\text{DFT}) - a(\text{XRD})]$: (a) with DFT; (b) with DFT-D*. The XRD values are given on the top of each figure. The 6-31G(d,p) basis set was employed for all calculations.

3.B. Keto-enol energies

After investigating the geometrical structures, the effect of those methods on the relative energy of the keto and enol forms is analyzed (Table 2). Experimentally, only the enol form of PYV3 is observed, *i.e.* the enol form is more stable than the keto one. The relative energy, $\Delta E_{KE} = E(K) - E(E)$, is thus expected to be positive. Table 2 shows the relative energies computed with the selected XCFs. Although ΔE_{KE} varies significantly depending on the XCF, all DFT values are positive, ranging from 3 to 13 kJ/(mol of asymmetric unit), in agreement with experiment. When adding dispersion energy, the keto form is more stabilized than the enol one so that the relative ΔE_{KE} energy gets less positive, if not negative like in the case of PBE and PBEsol [-2.5 and -2.7 kJ/(mol asym. unit) for DFT-D and -1.3 and -1.9 kJ/(mol asym. unit) for DFT-D*, respectively]. Since we know from experiment that ΔE_{KE} is positive, these two XCFs are not considered any further. DFT-D values, ranging from 2.7 to 10.2 kJ/(mol asym. unit), vary little from the DFT-D* ones (ranging from 3.4 to 9.9 kJ/(mol asym. unit)). Still, as expected, the dispersion energies obtained with DFT-D are larger than with DFT-D*, which favors the keto form thus decreasing the relative energy ΔE_{KE} (with the exception of ω B97X). The K/E Boltzmann distributions at 298.15K are then analyzed to further quantify the effects of the dispersion energy. In the case of ω B97X, barely no change is observed, with keto population increasing from 1% with DFT to 2% with DFT-D/D*. The effects are much larger for the other functionals, and they correspond to at least a 10% increase of the keto form upon adding dispersion, *i.e.* from 1% to 14% for PBE0, from 3% to 25% for B3LYP, and from 5% to 20% for PBEsol0.

Table 2. Keto-enol energy differences [$\Delta E_{KE} = E(K) - E(E)$, in kJ/(mol asym. unit)] as calculated with different XCFs for PYV3. The 6-31G(d,p) basis set was employed in all calculations.

Method	DFT	DFT-D	DFT-D*
B3LYP	8.3	2.7	3.4
PBE	2.6	-2.5	-1.3
PBE0	11.0	4.5	5.3
PBEsol	1.0	-2.7	-1.9
PBEsol0	7.1	3.4	4.0
ω B97X ¹	12.9	10.2	9.9

¹ TOLINTEG = 7 7 7 7 16

4. Conclusions

Density functional theory has been challenged for the geometry optimization of molecular switches in their solid crystalline state. By performing comparisons with XRD data, a recent contribution [10] has demonstrated that the HSEsol [12], PBEsol0, and ω B97X [11] can already be effective but, in this work, one has questioned whether the addition of empirical dispersion energy, as proposed by Grimme [13], could not further improve these results. First, we have shown that the use of the original dispersion parameters (DFT-D) overcontracts the unit cell for the selected XCFs (B3LYP [16], PBE [17], PBE0 [18], PBEsol [19], PBEsol0, and ω B97X). On the other hand, the down-scaled parameters proposed for the solid state (DFT-D*) [14] decrease this effect so that the B3LYP, PBE, and PBE0 XCFs achieve, for the unit cell volume, a rather good agreement with X-ray diffraction (XRD) data, though, mostly due to error compensations. Looking at the molecular geometries, the main conclusions are i) the inclusion of dispersion energy has almost no effect on the bond lengths, though systematically underestimating (overestimating) the length of the single (double) bonds, with the maximum difference between DFT and DFT-D* attaining 3 mÅ; ii) the valence angles are also barely affected when using DFT-D* compared to DFT with relative errors with respect to XRD data of 2% or less in both cases; and iii) in the case of the torsion angles, the use of DFT-D* XCFs improves the results since the variations with respect to XRD data are less spread out. The average errors with DFT-D* are of the order of 1° whereas with the DFT ones, only the PBEsol, PBEsol0, and ω B97X XCFs perform well. This means that an accurate description of the unit cell parameters leads to accurate molecular torsions but that accurate molecular torsions do not constitute a sufficient condition to fully describe the intermolecular interactions, and to reproduce the XRD unit cell. Finally, for all XCFs, the relative keto-enol energies ΔE_{KE} have been calculated, showing that the inclusion of dispersion stabilizes more the keto form than the enol one. As a consequence, the PBE and PBEsol XCFs incorrectly predict that the keto form is the most stable. On the other hand, with the exception of ω B97X, the other functionals predict a decrease of ΔE_{KE} but it remains positive. All these results and conclusions tend to argue that the PBEsol0 and ω B97X XCFs are reliable to predict molecular crystal structures and that there is no clear advantage of using empirical energy dispersion corrections as they were originally proposed [13] or later reparameterized for solids [14].

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Conflicts of Interest: “The authors declare no conflict of interest.”

References

1. *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R. J., Eds.; Plenum.; Springer US: New York, USA, 1998; ISBN 978-0-306-45882-8.
2. Kawata, S.; Kawata, Y. Three-Dimensional Optical Data Storage Using Photochromic Materials. *Chem. Rev.* **2000**, *100*, 1777–1788, doi:10.1021/cr980073p.
3. Hadjoudis, E.; Mavridis, I. M. Photochromism and thermochromism of Schiff bases in the solid state: structural aspects. *Chem. Soc. Rev.* **2004**, *33*, 579–588, doi:10.1039/b303644h.
4. Amimoto, K.; Kawato, T. Photochromism of organic compounds in the crystal state. *J. Photochem. Photobiol. C Photochem. Rev.* **2005**, *6*, 207–226, doi:10.1016/j.jphotochemrev.2005.12.002.

5. *Molecular Switches: Second, Completely Revised and Enlarged Edition*; Feringa, B. L., Browne, W. R., Eds.; WILEY-VCH, 2011; ISBN 978-3-527-31365-5.
6. *Tautomerism: Methods and Theories*; Antonov, L., Ed.; Wiley-VCH, 2013; ISBN 978-3-527-33294-6.
7. *Tautomerism: Concepts and Applications in Science and Technology*; Antonov, L., Ed.; WILEY-VCH, 2016; ISBN 978-3-527-33995-2.
8. Padalkar, V. S.; Seki, S. Excited-state intramolecular proton-transfer (ESIPT)-inspired solid state emitters. *Chem. Soc. Rev.* **2016**, *45*, 169–202, doi:10.1039/C5CS00543D.
9. Ruggiero, M. T.; Gooch, J.; Zubieta, J.; Korter, T. M. Evaluation of Range-Corrected Density Functionals for the Simulation of Pyridinium-Containing Molecular Crystals. *J. Phys. Chem. A* **2016**, *120*, 939–947, doi:10.1021/acs.jpca.5b11458.
10. Quertinmont, J.; Carletta, A.; Tumanov, N. A.; Leyssens, T.; Wouters, J.; Champagne, B. Assessing Density Functional Theory Approaches for Predicting the Structure and Relative Energy of Salicylideneaniline Molecular Switches in the Solid State. *J. Phys. Chem. C* **2017**, *121*, 6898–6908, doi:10.1021/acs.jpcc.7b00580.
11. Chai, J.-D.; Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615, doi:10.1039/b810189b.
12. Schimka, L.; Harl, J.; Kresse, G. Improved hybrid functional for solids: The HSEsol functional. *J. Chem. Phys.* **2011**, *134*, 24116, doi:10.1063/1.3524336.
13. Grimme, S. Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27*, 1787–1799, doi:10.1002/jcc.20495.
14. Civalieri, B.; Zicovich-Wilson, C. M.; Valenzano, L.; Ugliengo, P. B3LYP augmented with an empirical dispersion term (B3LYP-D*) as applied to molecular crystals. *Cryst. Eng. Comm.* **2008**, *10*, 405–410, doi:10.1039/B715018K.
15. Dovesi, R.; Orlando, R.; Erba, A.; Zicovich-Wilson, C. M.; Civalieri, B.; Casassa, S.; Maschio, L.; Ferrabone, M.; De La Pierre, M.; D’Arco, P.; Noël, Y.; Causà, M.; Rérat, M.; Kirtman, B. CRYSTAL14: A program for the *ab initio* investigation of crystalline solids. *Int. J. Quantum Chem.* **2014**, *114*, 1287–1317, doi:10.1002/qua.24658.
16. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98*, 11623–11627, doi:10.1021/j100096a001.
17. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868, doi:10.1103/PhysRevLett.77.3865.
18. Adamo, C.; Barone, V. Toward chemical accuracy in the computation of NMR shieldings: the PBE0 model. *Chem. Phys. Lett.* **1998**, *298*, 113–119, doi:10.1016/S0009-2614(98)01201-9.
19. Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X.; Burke, K. Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces. *Phys. Rev. Lett.* **2008**, *100*, 136406, doi:10.1103/PhysRevLett.100.136406.
20. Feller, D. The role of databases in support of computational chemistry calculations. *J. Comput. Chem.* **1996**, *17*, 1571–1586, doi:10.1002/(SICI)1096-987X(199610)17:13<1571::AID-JCC9>3.0.CO;2-P.
21. Schuchardt, K. L.; Didier, B. T.; Elsethagen, T.; Sun, L.; Gurumoorthi, V.; Chase, J.; Li, J.; Windus, T. L. Basis Set Exchange: A Community Database for Computational Sciences. *J. Chem. Inf. Model.* **2007**, *47*, 1045–1052, doi:10.1021/ci600510j.
22. Carletta, A.; Buol, X.; Leyssens, T.; Champagne, B.; Wouters, J. Polymorphic and Isomorphic Cocrystals of a N-Salicylidene-3-aminopyridine with Dicarboxylic Acids: Tuning of Solid-State Photo- and Thermochromism. *J. Phys. Chem. C* **2016**, *120*, 10001–10008, doi:10.1021/acs.jpcc.6b02734.

