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### **Referee report on a PhD Thesis**

**The story of resorcinol crystals and a new perspective for stabilizing high-pressure polymorphs at ambient conditions**

by

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The doctoral dissertation tells the story of resorcinol, which is a simple molecule still used as an active pharmaceutical ingredient. In particular, the dissertation is devoted to structural research of a few crystalline forms of resorcinol including polymorphs and solvates studied by X-ray diffraction at extreme conditions. So, the study is part of the important and still up-to-date problems of molecular self-assembly in crystals and of structure of a solid state. Ms. Safari chose relatively difficult research technique with use of diamond anvil cell, which requires great care and persistence from the researcher. The Candidate carried out a series of X-ray diffraction experiments for the samples obtained during isovolumetric crystallization or at constant temperature conditions. It is worth noticing that She did not stop at examining the resorcinol itself, but tried to find additional information on the pressure stability of crystalline forms already known from the literature and new ones. This issue was solved by the idea of introducing an admixture to individual crystalline phases. Ms. Safari tested the concept for resorcinol as her main object of the thesis,

and also for imidazole, benzimidazole and 2-methylbenzimidazole. The choice was not accidental, as the aforementioned chemicals are known to have high-pressure polymorphs.

The dissertation sent to me for review has a short form, permitted by Polish law on the basis of regulations (art. 187, Act of 20 July 2018, The Law on Higher Education and Science), and consists of a compendium of knowledge about resorcinol, which is also a guide to the accompanying publications. Presented results were published in three papers and they have appeared in very good international journals (two of them in *Cryst. Growth Des.* in 2019 and 2020 and one in *J. Phys. Chem. C.* in 2021). As required by law, formal statements of the co-authors are included in the thesis and it follows from them that Ms. Safari's contribution to the work is significant, 80 % for each article. Total and mean impact factor are equal to 12.28 and 4.09, respectively. The articles were cited 9 times until February 23, 2022 (Scopus), excluding self-citations. H-index of Ms Safari is 3 and results from Her 8 total number of scientific articles cited by 28 documents. Unfortunately, a list of conferences and other scientific activity is not mentioned in the dissertation, but despite the lack of them I assess the scientific activity of the Candidate as good. Since the articles were already reviewed during the peer-review process in each journals, it can be concluded that the idea for research work on resorcinol and the results have been thoroughly assessed. Nevertheless, in fulfilling my role as a reviewer, I have to look at the dissertation as a whole. It is part of a really long history that began in 1936 and never seems to end, and I consider Ms. Safari contribution to the mysterious world of resorcinol to be very significant. In my opinion, the main achievements are:

- (i) detailed determination of the p-T phase diagram for resorcinol obtained by careful and time-consuming studies by single-crystal X-ray diffraction with the use of diamond anvil cell,
- (ii) discovery and crystal structure determination of new high-pressure polymorph  $\zeta$  and new solvates of resorcinol as well as determining the conditions of their formation,
- (iii) showing that the doping pressure concept can be successfully employed for recovery and stabilization of high-pressure polymorphs at ambient conditions.

I have a few comments/remarks to thesis:

- (i) To paraphrase a question from a recent work on 2-chloro-4-nitroaniline polymorphs that really comes from much earlier, I would like to ask *Quo vadis, resorcinol?* In other words, I would like to know the Candidate's opinion on the problems related to the resorcinol phases that are still worth solving, if any.
- (ii) The Candidate used relatively high amount of dopants, for instance 15 and 25 wt %. Is there any clearly defined limit value of the mole fraction of the dopant when the dopant ceases to be a dopant and becomes an important element of the crystal structure treated as equal to the molecules of the parent structure?
- (iii) Page 18, Figure 8b: The figure shows a red-shift of the R1 and R2 bands assigned to the spin-forbidden d-d transition in the Cr<sup>3+</sup> ion induced by increasing pressure. The scale range is incorrect and it should be 690-700 nm.
- (iv) Page 54: Comparison of the data in Table 1 and Appendix C shows that the lattice parameter *b* for the  $\beta$  phase increases in the pressure range 0.5-0.91 GPa. Does it mean that this phase has linear negative compressibility?

Overall, I think the work sent to me for review contains a very rich, original and consistent research material. In my opinion, the Thesis is very valuable and meets the customary and statutory requirements for doctoral dissertations (art. 187, Act of 20 July 2018, The Law on Higher Education and Science). Therefore, I recommend that it is admitted to the next stages of the procedure for awarding the doctoral degree. I believe that this is one of the better planned and completed PhD theses in small molecule crystallography known to me. Additionally, I hereby submit an application for the award of Ms. Safari's doctoral dissertation especially for detailed determination of the p-T phase diagram for resorcinol and for the studies on stabilization of high-pressure polymorphs at ambient conditions also carried out for compounds outside the main topic of the dissertation.

*Manel Datchevska*