Comment on "trimorphs of 4-bromophenyl 4-bromobenzoate. Elastic, brittle, plastic" by S. Saha and G. R. Desiraju,

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Comment on "Trimorphs of 4-bromophenyl 4-bromobenzoate. Elastic, brittle, plastic" by S. Saha and G. R. Desiraju, *Chem. Commun.*, 2018, 54, 6348†

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A re-refinement of the published but chemically implausible, crystal structure of "Form III" of 4-bromophenyl 4-bromobenzoate shows that it is not a polymorph, but instead a co-crystal containing both 4-bromophenyl 4-bromobenzoate (≈25%) and likely 4-bromophenyl 4-nitrobenzoate (≈75%).

In *Chem. Commun.*, 2018, **54**, 6348-6351, Saha and Desiraju reported differences in flexibility of three polymorphs of 4-bromophenyl 4-bromobenzoate.[1] 'Form III' caught our attention as this polymorph was only observed in "very small" quantities under highly specific conditions and there is a complete absence of accompanying characterisation data other than a crystal structure. The crystal structure of 'Form III' is refined with a disorder model for one of the bromine atoms (Br(2)), which was stated to be "disordered about three positions" (Br(2), Br(3) and Br(4)). When we reviewed the structural model presented we immediately noted some severe issues relating to chemical plausibility of the reported crystal structure: firstly, the C(6)–C(1)–Br(3) and the C(2)–C(1)–Br(4) angles are 90.8(7)° and 91.4(7)°, respectively. The bond angles would be expected to be significantly closer to 120° given the sp^2 hybridisation of the phenylene carbons. Secondly, the disorder-modelled C(1)–Br(3) bond length is 2.296(15) Å and the C(1)–Br(4) bond length is 2.301(16) Å. Both of these are significantly longer than what would be expected for an aromatic bromine (≈1.9 Å). Thirdly, the thermal ellipsoids are abnormally large for the disordered region (some thermal parameters > 0.1) while there is no apparent disorder in the aromatic ring. These factors are not consistent with the presence of a

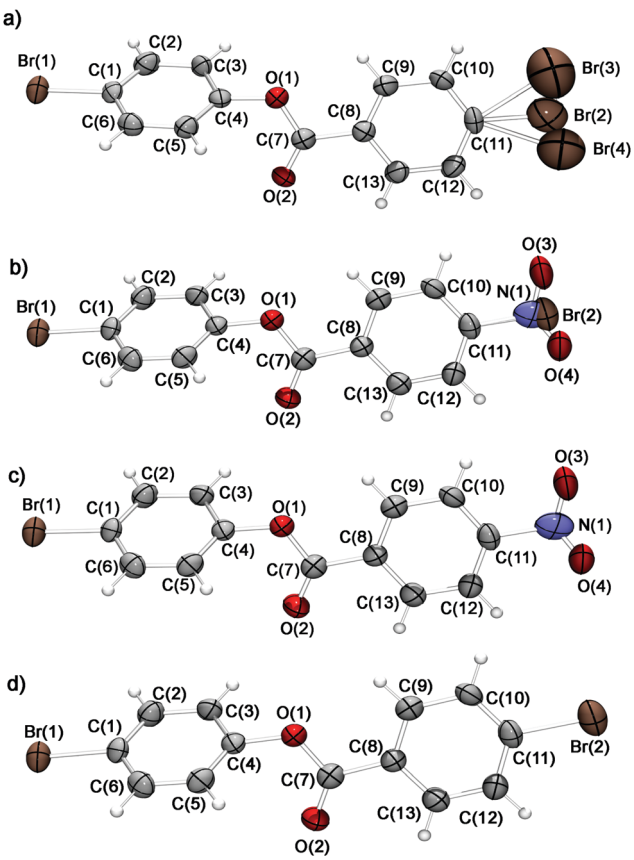

Fig. 1 ORTEP[2] representation of the Saha and Desiraju crystal structure: (a) as published as 4-bromophenyl 4-bromobenzoate; (b) newly refined as a co-crystal of 4-bromophenyl 4-bromobenzoate (25%) and 4-bromophenyl 4-nitrobenzoate (75%); (c) the 4-bromophenyl 4-nitrobenzoate part; (d) the 4-bromophenyl 4-bromobenzoate part. Atoms are shown as 50% probability thermal ellipsoids.

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disordered bromine atom. As such, we conducted a new refinement of the data, using the data deposited with the CCDC (Fig. 1).† This new refinement has improved refinement statistics compared to the published model (*e.g.* R_1 = 4.55% *vs.* 5.67%), and all bond lengths and angles are chemically reasonable.

Our analysis shows that 'Form III' is in fact a co-crystal containing both the reported 4-bromophenyl 4-bromobenzoate ($\approx$25%) and another component ($\approx$75%). This additional component appears to be 4-bromophenyl 4-nitrobenzoate and indeed the cell parameters of 'Form III' match those of the crystal structure of this compound, which was reported in 2017 by the same authors.[3] Some simple spectroscopic measurements such as FTIR would have readily identified the presence of the NO_2 group or any other impurities present in the sample.

Given that the authors use the presence and absence of certain supramolecular interactions within this crystal structure as justification for the mechanical properties of the entire polymorph series of 4-bromophenyl 4-bromobenzoate, this calls into question many of the conclusions drawn in this paper. Our model unambiguously demonstrates that the conclusions of the paper cannot be sustained as the structural model and chemical identity of the compound is incorrect.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

1 S. Saha and G. R. Desiraju, *Chem. Commun.*, 2018, **54**, 6348–6351.
2 L. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.
3 S. Saha and G. R. Desiraju, *J. Am. Chem. Soc.*, 2017, **139**, 1975–1983.