

Comments on the elusive crystal structure of 4-iodo-4'-nitrobiphenyl

Norberto Masciocchi,^{*a} Mirka Bergamo^b and Angelo Sironi^{*a}

^a Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università di Milano, via Venezian 21, 20133, Milano, Italy

^b Dipartimento di Chimica Inorganica, Metallorganica ed Analitica, Università di Milano, via Venezian 21, 20133 Milano, Italy

The recently proposed crystal structure of 4-iodo-4'-nitrobiphenyl is here confirmed on the basis of experimental diffraction data on single crystals and powders of high crystallinity; a reinterpretation of the nature of the (faulted) material studied in the original paper is also presented.

In a recent issue of *Chemical Communications*, Sarma *et al.* (hereafter, Sarma) reported¹ the design, based on the strength of Ar–NO₂...I–Ar interactions, of a new crystal phase, possessing second harmonic generation (SHG) properties. It was reported therein that single-crystal X-ray diffraction (XRD) on two crystals of 4-iodo-4'-nitrobiphenyl (INB) with different morphology (obtained by recrystallization from benzene or nitromethane) afforded, in both cases, an F-centered orthorhombic lattice, but no reliable structural model; accordingly, it was suggested that all samples chosen for single-crystal analysis were flawed, since the ordered structural model, obtained by the combination of XRD (cell/space group), semiempirical quantum chemistry calculations (molecular conformation), crystallochemical considerations (approximate location) and constrained lattice energy minimisation (final coordinates), did not match the observed intensity data.¹

Sarma found that INB molecules form polar ribbons running along [001] through robust Ar–NO₂...I–Ar interactions (a well defined² supramolecular synthon³); however, in contrast with such robustness, the features observed in the XRPD pattern were modelled by a significant small-particle-size broadening effect along [001] (with an average coherent domain of 50 Å, accounting for three INB molecules only!). Suspecting a two-dimensional polytypic behaviour like that found in (C₅Me₅)ReO₃,⁴ we decided to reconsider the INB problem by coupling XRPD, computer simulation of faulted crystals and conventional 'single-crystal' X-ray diffraction.

We have synthesized INB as described in refs. 1 and 5, and found that the reaction product is, according to GC–MS, a mixture of INB and of the symmetrically substituted dinitro (DNB) and diiodo-biphenyls (DIB), in an approximate 90:9:1 ratio, while in the XRPD pattern only the two major phases (INB and DNB) could be recognized. Recrystallization from benzene, nitromethane or hexane eventually afforded only one crystal phase (INB, although, according to GC–MS, traces of DNB were still present), whose XRPD pattern revealed a well crystallized system with no anisotropic broadening (FWHM < 0.2° 2θ). It was of note that our XRPD data (Fig. 1) can be

indexed with the published INB cell parameters but show an intensity distribution different from that reported in Fig. 2 of ref. 1; in particular, two, previously unobserved, intense low angle peaks are now present.

Recrystallization from nitromethane spontaneously afforded light yellow INB crystals of very good quality, whose structure was easily solved and successfully refined in space group *Fdd2* on data from two different crystals (which were found to differ only in the amount of racemic twinning present: none for crystal 1 and [73:27] for crystal 2).[‡] The derived structural model is very similar to that proposed in ref. 1 and, allowing a rather good match (*R_p* = 0.10) between observed and calculated XRPD data (see Fig. 1), it correctly describes also the bulk. Accordingly, INB can afford highly crystalline samples.

In spite of our efforts, we were unable to prepare the poorly crystalline phase originally reported as INB. Nevertheless, we would like to tentatively propose, in the absence of direct experimental data, two possible explanations for Sarma's observations.

The substitution of one INB molecule by DNB generates an unstrained faulted ribbon, as schematically shown in Fig. 2, which, despite the inversion of the NO₂...I link, possesses fully ordered C and H atoms (note that DIB could act in the same manner while the copresence of DIB and DNB allows for any number of faults). The insertion of a single DNB molecule per

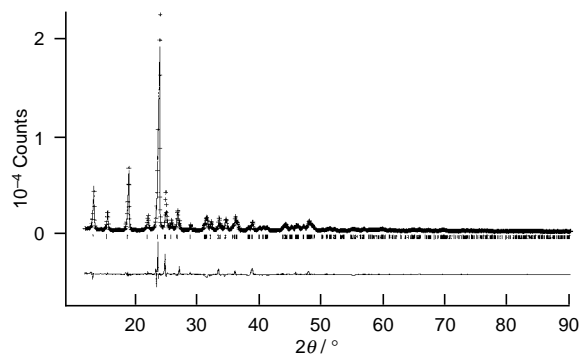


Fig. 1 Rietveld refinement plot of the INB phase with peak markers and difference plot at the bottom. Note that the first two log-angle peaks are consistent with the structural model and do not require any anisotropic broadening correction in order to spread their intensity into the background.

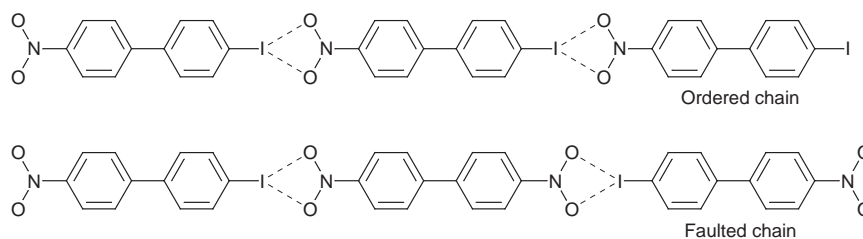


Fig. 2 Schematic drawing of the polarity inversion of one INB chain in the presence of a single DNB molecule per chain (conditioned disorder). Note that at most one DNB molecule can fit in an INB chain; DIB would act in the same manner, while the simultaneous presence of DIB and DNB allows for any number of faults (up to a random disorder).

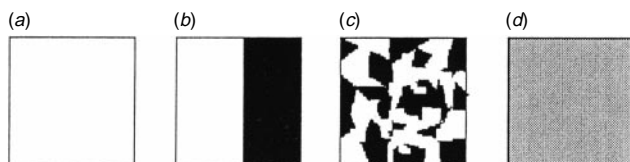


Fig. 3 Schematic drawing of the tiling of the *ab* plane of INB crystals with black and white dots (for up and down polar INB chains, respectively), showing a polar single crystal (*a*), a racemic (macro)twin (*b*), a faulted paracrystal with many twin boundaries (*c*) and a fully disordered *Fddd* (microtwinning) phase (*d*)

chain behaves similarly to a single error in the stacking sequence of pure INB which, however, would induce some strain. This kind of fault, as shown by Hulliger *et al.* for the 1,4-nitrophenylpiperazine–perhydrotriphenylene inclusion compound,⁶ may evolve into a 180° [001] twinned macrostate with a fuzzy interface whose size depends on their intrinsic probability. However, since high error frequencies imply small interfaces, sharp XRPD peaks and possible SHG effects (while, low, non-zero probabilities lead to large ‘interfaces’, broad XRPD peaks and no SHG), the presence of DNB (or of less likely INB inversion faults) can be taken as responsible for all experimental evidences only if crystals of intermediate nature occur.

Alternatively, since inversion of the polarity of a whole (ordered) chain marginally affects the overall packing (more or less like an inversion fault, which inverts only ‘half’ a chain), Sarma’s specimen may consist of a two-dimensional polytypic phase with (randomly distributed) microdomains of inverse polarity, large enough to guarantee SHG properties, but ‘flawing’ the original X-ray analysis, much like what is found for solid (C₅Me₅)ReO₃.⁴ Indeed, juxtaposition of antiparallel domains in the *ab* plane can afford, on lowering the size of the homopolar regions, (*a*) untwinned *Fdd2* single crystals (our crystal 1); (*b*) racemic (macro)twin (crystal 2); (*c*) two dimensional polytypes (Sarma’s specimen); (*d*) disordered (*i.e.* microtwinning) *Fddd* ‘single’ crystals (Fig. 3). Since cases (*a*) and (*b*) would lead to sharp XRPD features and case (*d*) cannot be SHG active, only case (*c*) fits Sarma’s experimental observations. That 2D polytypic crystals from different preparations may have different ‘structures’ should not surprise, particularly after it has been shown that crystals from the same batch and even different portions of the same good looking ‘single’ crystal may possess different peak intensities, reflecting the different ratio of ordered *vs.* disordered (*i.e.* boundary) regions.⁴

Summarizing, single-crystal and powder diffraction analyses of INB afforded an unambiguous crystal structure with long polar ribbons of INB molecules packed, in *Fdd2*, in a head-to-tail fashion, as originally inferred in ref. 1. This agrees well with the proposed robustness of the NO₂–I synthon, which has been

extensively used in devising supramolecular assemblies of organic molecules.⁷ Unfortunately, even if the outcome of the work reported by Sarma *et al.* happens to match the true INB crystal structure, the nature of their material (single crystals and bulk) remains obscure.

We acknowledge the Italian MURST and CNR (CSSMTBO) for funding. The courtesy of Dr G. A. Arduozia, who ran the GC–MS measurements, is also acknowledged. We also thank Professor A. Gavezzotti for helpful discussions.

Notes and References

† E-mail: angelo@csmtbo.mi.cnr.it

‡ *Crystal data*: C₁₂H₁₀INO₂, *M* = 325.10; orthorhombic, space group *Fdd2*, *a* = 8.200(4), *b* = 18.887(4), *c* = 14.385(15) Å, *U* = 2228(3) Å³, *D_c* = 1.938 g cm⁻³; Single crystal results (crystal 1 and, in parentheses, crystal 2); CAD4, graphite monochromated Mo-Kα radiation, solution by Patterson and difference Fourier methods; refinement by full-matrix least squares, SHELX93⁸), *R*₁ and *wR*₂ = 0.014 (0.019) and 0.032 (0.044), respectively, for 567 (971, due to the presence of Friedel pairs) independent observed reflections [*I* > 2σ(*I*)] collected in the 3 < θ < 26° (25°) range. Powder diffraction data (RIGAKU D-III/MAX, graphite monochromated Cu-Kα radiation, refinement by GSAS⁹), *R_p*, *R_{wp}* and *R_F* = 0.104, 0.144 and 0.085, respectively, for 3901 data collected in the 12 < 2θ < 90° range (252 reflections). CCDC 182/877.

§ The explicit Fourier transform of such a model, computed with the aid of DISCUS on 20 × 20 × 20 cells (about 1 000 000 non-hydrogen atoms),¹⁰ afforded some diffuse scattering and markedly asymmetric (111) or split (022) peaks; all these features are consistent with the broadening and lowering of peak intensity observed in Sarma’s powder pattern.

- 1 J. A. R. P. Sarma, F. H. Allen, V. L. Hoy, J. A. K. Howard, R. Thaimattam, K. Biradha and G. R. Desiraju, *Chem. Commun.*, 1997, 101.
- 2 F. H. Allen, B. S. Goud, V. J. Hoy, J. A. K. Howard and G. R. Desiraju, *J. Chem. Soc., Chem. Commun.*, 1994, 2729; V. R. Thalladi, B. S. Goud, V. J. Hoy, F. H. Allen, J. A. K. Howard and G. R. Desiraju, *Chem. Commun.*, 1996, 401.
- 3 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
- 4 N. Masciocchi, P. Cairati, F. Saiano and A. Sironi, *Inorg. Chem.*, 1996, **35**, 4060.
- 5 J. Harley-Mason and F. G. Mann, *J. Chem. Soc.*, 1940, 1379.
- 6 J. Hulliger, P. Rogin, A. Quintel, P. Rechsteiner, O. König and M. Wübbenhorst, *Adv. Mater.*, 1997, **9**, 677; O. König, H. B. Bürgi, T. Armbruster, J. Hulliger and T. Weber, *J. Am. Chem. Soc.*, 1997, **119**, 10 632.
- 7 F. H. Allen, J. P. M. Lommerse, V. J. Hoy, J. A. K. Howard and G. R. Desiraju, *Acta Crystallogr., Sect. B*, 1997, **53**, 1006 and references therein.
- 8 G. M. Sheldrick, SHELX93; Program for the refinement of crystal structures, University of Göttingen, 1993.
- 9 A. C. Larson and R. B. Von Dreele, GSAS, Generalized Structure Analysis System, LANSCE, Ms-H805, Los Alamos National Laboratory, New Mexico, 1994.
- 10 R. B. Neder and T. Proffen, *J. Appl. Crystallogr.*, 1996, **29**, 727.

Received in Cambridge, UK, 19th February 1998; revised manuscript received 8th May 1998; 8/034861