Commensurate Urea Inclusion Crystals with the Guest (*E,E*)-1,4-Diiodo-1,3-Butadiene.

Amanda F. Lashua[†], Tiffany M. Smith[†], Hegui Hu[‡], Lihui Wei[□], Damian G. Allis[†], Michael B. Sponsler[†] and Bruce S. Hudson[†]*

[†]Department of Chemistry, Syracuse University, Syracuse, NY 13244-4100

[‡] Current address: Advanced Biotech Inc., 10 Taft Road, Totowa, NJ 07512

[□]Current address: Nordion, Inc. 447 March Road, Ottawa, ON, K2K 1X8, Canada and Division of Cardiology, University of Ottawa Heart Institute, 40 Ruskin Street, Ottawa, ON K1Y 4W7, Canada.

*email: bshudson@syr.edu

Supplemental Information

General Information

All reagents were used as received unless otherwise stated. They were obtained from Sigma-Aldrich, Alfa Aesar, and Fisher Scientific. Crystallographic data for all compounds was collected on a Bruker KAPPA APEX DUO diffractometer using Mo-K_α radiation (λ = 0.71073Å) containing an APEX II CCD system.[1] The data was corrected for Lorentz and polarization[2] effects, and adsorption corrections were made using *SADABS*.[3] Structures were

solved by direct methods. Refinements for each structure were carried out using the SHELXTL[4] crystallographic software. Following assigning all non-hydrogen atoms, the models were refined against F^2 first using isotropic and then using anisotropic thermal displacement parameters. The hydrogen atoms were introduced in calculated positions and then refined isotropically. Neutral atom scattering coefficients along with anomalous dispersion corrections were taken from the *International Tables*, Vol. C.

DIBD Synthesis

DIBD was synthesized using a published procedure with slight modifications to better protect the reaction and product from air and light.[5] The product identity was confirmed by comparing ^{1}H NMR to the literature data.

Crystallization of DIBD:UIC by slow cooling method

Urea was dissolved in methanol (5 mL, 1.8-2.0 M) and degassed (by N_2 bubbling). This septum-capped solution was introduced in the glovebox where the recently prepared DIBD was added (in either a 1:5 or 1:6 DIBD:urea mol ratio). The solution was then transferred into a 5 mL amber ampoule and flame sealed under vacuum. This sample was placed in an antifreeze bath at 25 ^{0}C with a stepping motor attached to the temperature control dial in order to reduce the temperature at a set rate (0.3-1.0 ^{0}C/ hour) until the temperature reached -20 ^{0}C. The ampoules were promptly removed and opened. The mother liquor was removed quickly to prevent dissolution of the crystals as the solution warmed. The crystals were a pale yellow color ranging from powder-like crystals to coarse clusters of needle-like crystals. The crystals were sorted using CCl_4 to separate the UICs, those that sank, from tetragonal urea, those that floated, resulting in a small amount of tetragonal urea and mostly UICs.

Crystallization of DIBD:UIC slow evaporation method

A solution of urea (1.8M) and DIBD (in a 1:5 mole ratio DIBD:urea) was made in methanol. The solution was then diluted up to 4 times the initial volume and poured into a glass Petri dish. This dish was placed in a modified vacuum tight plastic container. The container was placed in a freezer at 0^{o} C with argon flowing at a constant rate (single bubble every few seconds) into the sealed container through one of the two holes drilled into the lid. A bubbler was attached to the second hole for the exit line and the solution left for up to 3 weeks to allow for slow evaporation of the solvent. The resulting crystals were collected from the container. The crystals were sorted using CCl_4 to separate the UICs from tetragonal urea resulting in long needle-like UICs.

References

1 APEX II, Data Collection Software, version 2011.8-0; Bruker AXS Inc.: Madison, WI, **2005-2011**.

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3 Sheldrick, G. M. SADABS; University of Göttingen: Göttingen, Germany, **1996**.

4 SHELXTL PC, version 6.12; Bruker AXS Inc.: Madison, WI, **2002**.

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