Significance: Perylene derivatives find applications in organic electronics as electron-transport materials. Now, a facile three-step synthesis of 7,8,15,16-tetraazaterrylene opens the door for higher ryles which have not been studied as extensively. Knoevenagel condensation of phenalene-1,3-dione (1) with lauric aldehyde is followed by a Michael addition of a second molecule of 1 to give 2. This is heated in neat trifluoroacetic acid effecting the cyclodehydration to 3.

Comment: The last step is a domino reaction with hydrazine that produces tetraazaterrylene 6 while the solubilizing alkyl chain is expelled as a hydrazone. A mechanism for the domino reaction has been proposed by Tu (Org. Biomol. Chem. 2009, 7, 1171) and involves formation of diazepine 4 which would undergo a 3,3-sigmatropic rearrangement to form the transannular C–C bond (red). The use of a long-chain aliphatic aldehyde is deliberate – it ensures solubility of 2 and 3 and favors the formation of the tetraaza-product 6.