Diethylamine has been trapped in its less stable gauche conformation in a solvate of the title diol; the staggered conformation, which is ca. 4 kJ mol$^{-1}$ more stable, is found in another solvate of the same host.

Solvation is an entropically disfavoured process during crystallization, being observed in only around 15% of non-ionic organic compounds in the Cambridge Structural Database. More rare is when the crystal lattice of a solute molecule (host) traps a conformationally flexible solvent molecule (guest) in one of its higher energy conformations. In none of these cases, however, has a solvate with the solvent in a more stable conformation in the same host ever been reported. We report here the unprecedented observation of both gauche and staggered rotamers of diethylamine, 1a and 1b, in two distinct 1:1 solvates, 2a and 2b, of the host compound 1,5-dichloro-cis-9,10-diethynyl-9,10-dihydroanthracene-9,10-diol, 3. These solvates were isolated only after an analysis of the crystal structure of unsolvated 3, which is also reported in this communication.

Isolation of single crystals of 2a, 2b and 3 was achieved only with careful experimentation. Hydroxy ethynylation of 1,5-dichloroanthraquinone (TMSC=C=Cl, KOH) gave predominantly the trans-isomer, 4, with the amount of cis-isomer, 3, being so small that it could never be separated satisfactorily with chromatography. When the crude product was crystallized from 1:1 acetone–benzene, two different crystal morphologies were obtained, prisms, and needles, corresponding to the cis- and trans-isomers, 3 and 4, respectively. In the cis-diol 3 (Fig. 1), one of the hydroxyl groups forms an intramolecular O–H···Cl–C hydrogen bridge ($D_1$ 3.04 Å, $d$ 2.32 Å, $\theta$ 129°), while the other donates to an intermolecular O–H···π interaction (3.44 Å, 2.78 Å, 144°; to triple bond midpoint), with some synthon features seen previously. There is an intermolecular C–H···O–H interaction (3.08 Å, 2.13 Å, 145°), and also an intermolecular C–H···Cl–C bridge (3.67 Å, 2.72 Å, 146°). However, there is no evidence of an O–H···O hydrogen bond.

We had noted previously, that an awkward hydrogen bond pattern in trans-diol 4 results from the sterically constrained environment of hydroxyl and ethynyl groups, and that this uncomfortable pattern can relax via solvation. Noting further that the packing in cis-diol 3 is reminiscent of that in 4, we crystallized the crude mixture of isomers from Et$_2$NH, since organic bases were found to promote solvation very effectively. Crystals with different morphologies, cuboid and plate-like, were again obtained and two different crystals from this batch with clearly different unit cells were found to correspond to the 1:1 solvates 2a and 2b.† Fig. 2 shows the conformations (1a and 1b) of Et$_2$NH in solvates 2a and 2b. The dihedral angle between the two best planes in the gauche and staggered conformers is 70 and 171°, respectively. In all seven Et$_2$NH solvates in the Cambridge Structural Database (version 5.25, November 2003), the molecule adopts the more stable staggered conformation. The energy difference between the staggered and the gauche conformations was estimated to be 3.26 kJ mol$^{-1}$ (DFT) and 5.06 kJ mol$^{-1}$ (HF). In order to obtain a rationale as to why the two crystal forms were obtained, the packing in these forms was examined more carefully.

The role of solvent in improving the hydrogen bond arrangement in 3 is without doubt. In solvate 2a (Fig. 3), the (gauche) Et$_2$NH···O interactions are

![Fig. 1 Crystal structure of cis-diol 3.](image1.png)

![Fig. 2 Gauche, 1a, (left) and staggered, 1b, (right) conformations of Et$_2$NH in solvates 2a and 2b.](image2.png)

![Fig. 3 Crystal structure of solvate 2a.](image3.png)
molecule links the intramolecular hydroxyl groups of the diol and there is an infinite cooperative array of O–H⋯N (2.677 Å, 170.0°), N–H⋯O (3.178 Å, 2.19 Å, 166.4°) and O–H⋯O (2.762 Å, 1.81 Å, 170.5°) interactions. In solvate 2b too, the (staggered) Et₂NH molecule performs the same function (Fig. 4). The cooperative array is topologically the same but the metrics are different: O–H⋯N (2.709 Å, 1.72 Å, 175.5°); N–H⋯O (3.350 Å, 2.39 Å, 156.8°); O–H⋯O (2.764 Å, 1.78 Å, 173.9°). While the O–H⋯N and O–H⋯O interactions are comparable in 2a and 2b, the N–H⋯O bridge is distinctly longer in 2b (interaction e is longer than interaction b). This lengthening of the N–H⋯O interaction seems to arise from steric hindrance between one of the ethyl groups of the solvent and the aromatic ring of the diol. When the methyl fragment in this ethyl group swings away from the ring in the gauche conformation, steric hindrance is reduced and the N–H⋯O bridge can become shorter. We suggest that the N–H⋯O lengthening in 2b is balanced by the solvent being in its most stable staggered conformation. Alternatively, one might say that the more energetic gauche conformation is stabilized in solvate 2b by a better N–H⋯O hydrogen bond. All other packing features in the two solvates are nearly comparable and we feel that it is reasonable to define, given that it is the minor component in these solvates that has the conformational variations, is to refer to them as conformational pseudopolymorphs.13

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Notes and references

† Data were collected using a Bruker SMART 1K CCD area detector.

Crystal data for 2a: (C₁₈H₁₀Cl₂O₂)₂(C₂H₅N), M = 402.30, monoclinic, a = 8.1794(2), b = 13.648(4), c = 18.0272(5) Å, β = 90, β = 96.984(1), γ = 90°, V = 1997.53(9) Å³, T = 120(2) K, space group P2₁/n, Z = 1, μ(Mo-Kα) = 0.342 mm⁻¹, size 0.26 × 0.20 × 0.10 mm. 19 907 total reflections of which 3925 were independent, 3353 observed (I > 2σ(I)). Refinement against F² with 328 parameters, R₁ [I > 2σ(I)] = 0.0460. For 2b: (C₁₈H₁₀Cl₂O₂)₂(C₂H₅N), M = 402.30, orthorhombic, a = 14.955(3), b = 13.659(3), c = 19.433(4) Å, α = 90, β = 90, γ = 90°, V = 3969.4(14) Å³, T = 95(2) K, space group Pbcn, Z = 1, μ(Mo-Kα) = 0.344 mm⁻¹, size 0.22 × 0.18 × 0.06 mm. 41 925 total reflections of which 4557 were independent, 3359 observed (I > 2σ(I)). Refinement against F² with 328 parameters, R₁ [I > 2σ(I)] = 0.0565. For 3: C₁₂H₁₆Cl₂O₂, M = 329.16, monoclinic, a = 11.473(2), b = 12.5163(3), c = 16.2952(5) Å, α = 90, β = 100.56(1), γ = 90°, V = 1498.34(7) Å³, T = 120(2) K, space group P2₁/n, Z = 1, μ(Mo-Kα) = 0.436 mm⁻¹, size 0.24 × 0.22 × 0.14 mm. 16 656 total reflections of which 3431 were independent, 2430 observed (I > 2σ(I)). Refinement against F² with 239 parameters, R₁ [I > 2σ(I)] = 0.0460. CCDC 225589–225591. See http://www.rsc.org/suppdata/cc/b3/b316708f for crystallographic data in cif or other electronic format.

‡ The Et₂NH solvate of 4 was also isolated in this experiment: (C₄H₈O₂)₂(C₂H₅N), M = 402.30, triclinic, a = 8.8881(5), b = 9.5190(5), c = 10.6909(2), β = 116.003(2), γ = 90.739(2)°, V = 623.39(6) Å³, space group P1, Z = 0.5 and the O–H⋯N–H–O hydrogen bond pattern is similar to that in the aminophenol. See V. R. Vangala, B. R. Bhogala, A. Dey, G. R. Desiraju, C. K. Broder, P. S. Smith, R. Mondal, J. A. K. Howard and C. C. Wilson J. Am. Chem. Soc., 2003, 125, 14 495. The crystal structure of this solvate will be published elsewhere.