# An Intramolecular OH···π(arene) Interaction in a BINOL-Phenazine Cocrystal with a 'Free' N-Atom

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## Electronic Supporting Information

### Contents

## 1. Materials and Methods

All reagents were purchased from Sigma-Aldrich co. and used as received.

Powder X-ray data were collected on a *Rigaku* XD Ultima II diffractometer (Serial No. AD20971) equipped with a NaI scintillation detector using Cu *K*α radiation (λ=1.54056 Å).

Single crystal X-ray data were collected on on a Bruker APEX2 system at 100 K with graphite-monochromated Cu Kα radiation (λ = 1.54178 A). Data were obtained in four sets using omega–phi scans with omega steps of 0.5u and phi steps of 90u. The data were processed using SaintPlus. Corrections for Lorentz-polarisation effects were applied. Absorption was negligible. All structures were solved using direct methods that yielded the non-hydrogen atoms. All hydrogen atoms were located in Fourier-difference electron density maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms associated with carbon atoms were refined in geometrically constrained riding positions. Hydrogen atoms associated with oxygen atoms were included in the located positions and refined isotropically without constraints. Refinement was achieved using SHELX-97.

Thermal analysis of (R-BINOL)·(phen) was performed using Differential Scanning Calorimetry (DSC) (TA® Q2000 V 24.2). A sample of approximately 8 mg was weighed and hermetically sealed in an aluminum pan. Measurements for thermal events (ie., melting point) were obtained in a temperature range of 30 – 230 °C using a 20 °C/min heating rate.

A survey of the CSD (version 5.39, May 2017) was performed with ConQuest (version 1.19). For the survey regarding multi-component solids of BINOL, cocrystals were defined as molecules possessing hydroxyl substituents at 2- and 2'- positions on respective binaphthyl rings with no substitution at any or all other positions on the ring system. All structures were targeted to satisfy following criteria: (a) crystallographic R-factor < 0.10, (b) no metal coordination, (c) 3D coordinates fully determined, (d) refined hydroxyl hydrogen atom positions, and (e) a contact distance of < 4.0 Å between each BINOL O-H substituent and an intermolecular atom defined as any atom with an atomic mass less than Cl. The search resulted in 134 multi-component solids with BINOL (i.e. racemic and enantiopure) with only three structures (ref. codes: IHUWOX, PUZZIT, TAZLOW) that exhibit an O-H group that does not participate in a conventional O-H···X (X = O, N, S) H-bond. For the survey regarding phenazine cocrystals, the same criteria within ConQuest were maintained with the contact distance of < 4.0 Å between each phenazine 'N' atom and an intermolecular atom defined as any atom with an atomic mass less than Cl. A total of 79 multi-component solids were identified. A total of 20 structures were determined to exhibit a single N(phen) ring atom, similar to (R-BINOL)·(phen), that does not participate in a conventional H-bond.

## 2 *R-BINOL*·Phenazine Cocrystal

### 2.1 Synthesis of (*R-BINOL*)·(phen)

Enantiopure BINOL (> 99% ee.), phen (98%) and 2-propanol (HPLC grade, 99.9%) were used as received from Sigma-Aldrich®. Cocrystals of (*R*-BINOL)·(phen) were obtained by dissolution of equimolar amounts of (*R*)-(+)-BINOL (50 mg) and phen (32 mg) in 2-propanol (1 mL). Following slow evaporation, small rods of (*R*-BINOL)·(phen) suitable for single-crystal X-ray diffraction formed.

### 2.2 Powder X-ray diffractometry data

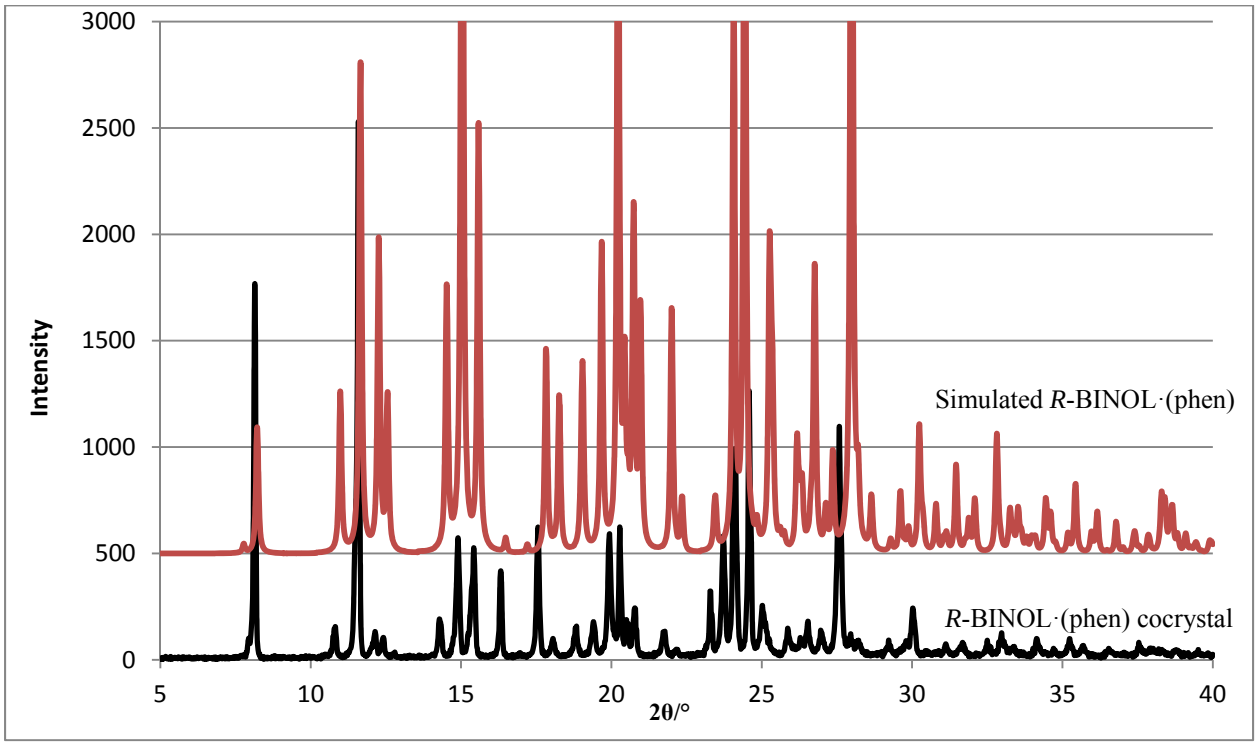


**Figure S - 1**. PXRD diffractogram of *R*-BINOL·(phen) cocrystal compared to simulated pattern. Simulated pattern peaks are shifted approximately +0.25 2θ/° relative to the experimental pattern.

## 2.3 Thermal Analysis Data

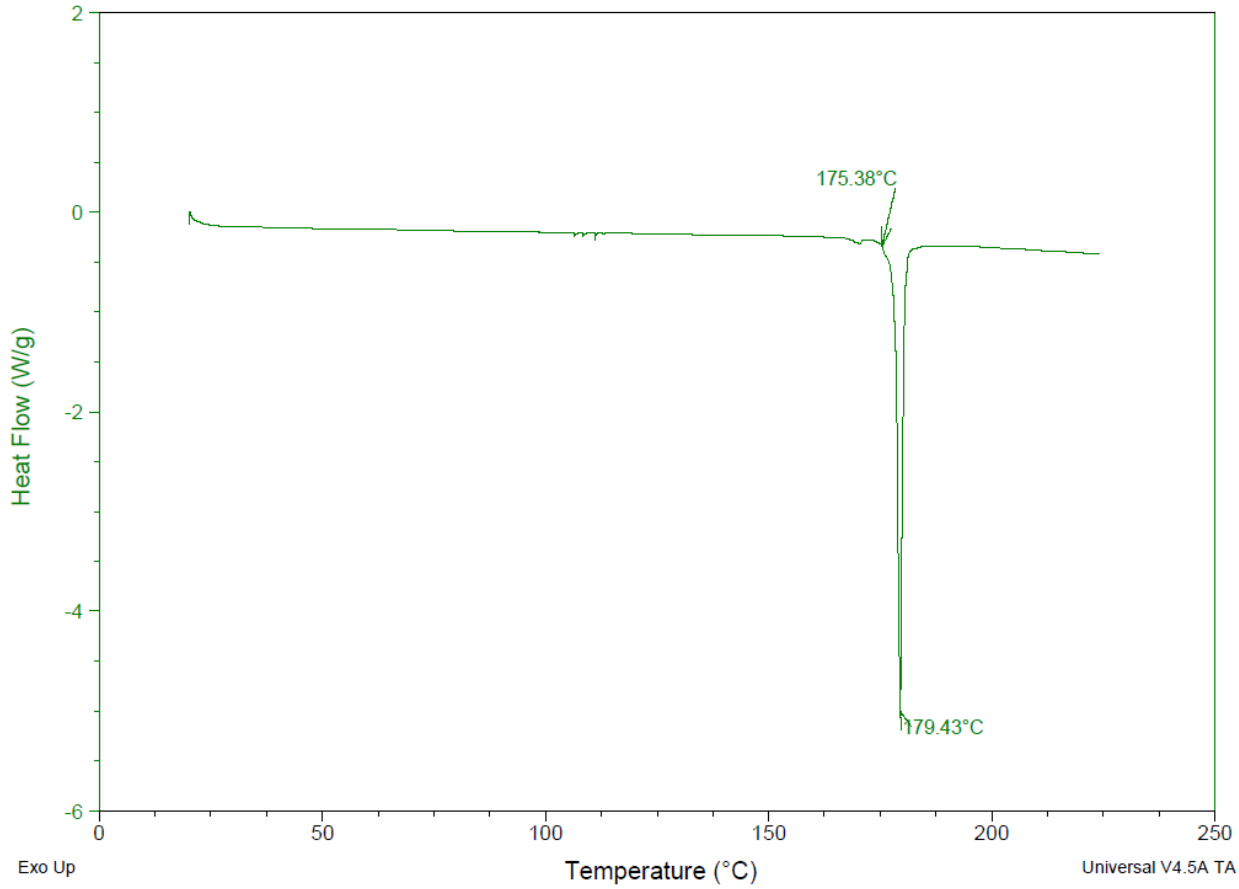


**Figure S - 2** Thermal analysis by DSC for *R*-BINOL·(phen). Onset of melt event at 175.4 °C with completion at 179.4 °C.

## 2.4 Thermal Analysis Data

| Compound | (*R*-BINOL)·(phen) |
|---|---|
| Formula | ($C_{32}H_{22}N_2O_2$) |
| Formula Weight | 320.5 |
| Crystal System | Monoclinic |
| Space group | $P2_1$ |
| *a*/Å | 10.7632(3) |
| *b*/Å | 9.3311(3) |
| *c*/Å | 11.3836(3) |
| α/° | 90.00 |
| β/° | 93.368(1) |
| γ/° | 90.00 |
| *V*/Å$^3$ | 1141.31 |
| Z | 2 |
| *T*/K | 100 |
| $D_c$ (g/cm$^3$) | 1.358 |
| $\mu$ (Cu $K_\alpha$) (cm$^{-1}$) | 0.674 |
| No. of reflns collected | 12930 |
| unique reflns | 3752 |
| $R_{int}$ | 0.0171 |
| Reflections with $I > 2\sigma(I)$ | 3684 |
| No. of params | 333 |
| $R(F)$, $F > 2\sigma$(F) | 0.0252 |
| w$R(F^2)$, $F > 2\sigma$(F) | 0.0630 |
| $R(F)$, all data | 0.0257 |
| w$R(F^2)$, all data | 0.0634 |
| Δr (max., min.) (e Å$^{-3}$) | 0.141-0.186 |
| Flack parameter | -0.02 (6) |

**3** *S*-BINOL·Phenazine Cocrystal.

## 3.1 **Synthesis of (*S-BINOL*)·(phen)**

Enantiopure BINOL (> 99% ee.), phen (98%) and 2-propanol (HPLC grade, 99.9%) were used as received from Sigma-Aldrich®. Cocrystals of (*S*-BINOL)·(phen) were obtained by dissolution of equimolar amounts of (*S*)-(—)-BINOL (50 mg) and phen (31 mg) in 2-propanol (1 mL). Following slow evaporation, small rods of (*S*-BINOL)·(phen) suitable for single-crystal X-ray diffraction formed.

## 3.2 Powder X-ray diffractometry data

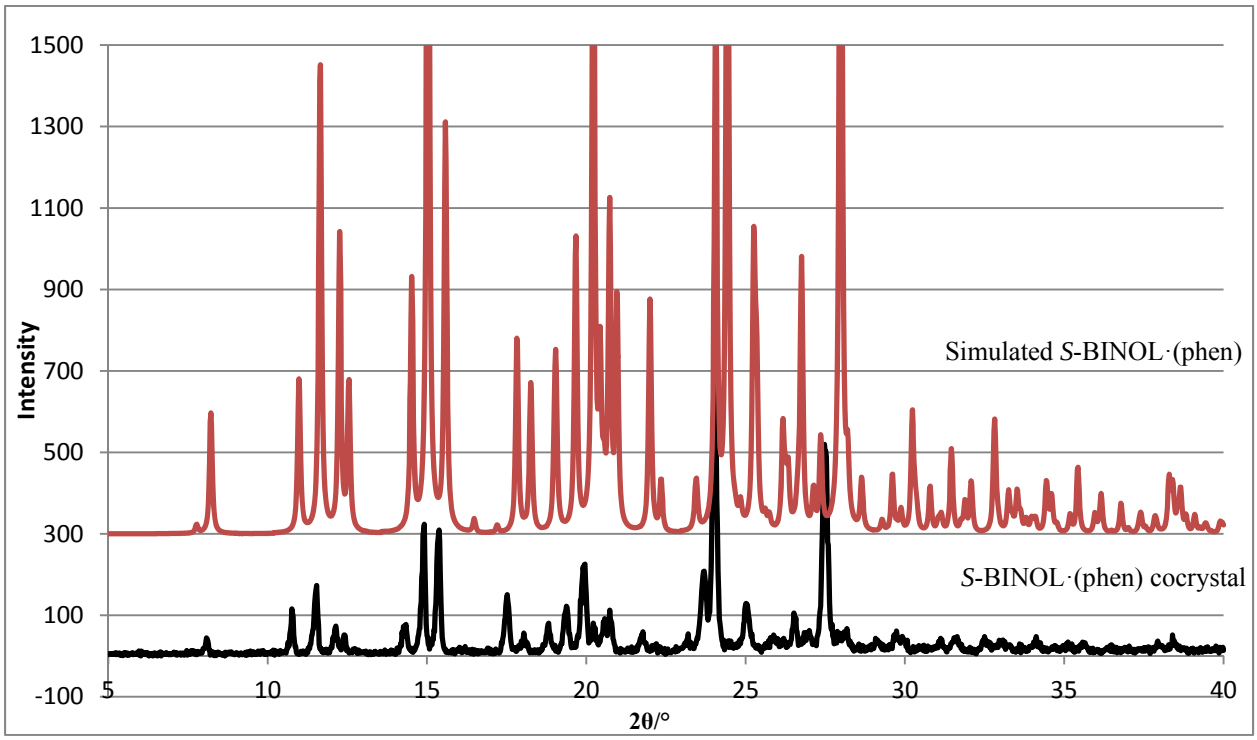


**Figure S - 3** PXRD diffractogram of *S*-BINOL·(phen) cocrystal compared to simulated pattern. Simulated pattern peaks are shifted approximately +0.25 2θ/° relative to the experimental pattern.