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**SINGLE CRYSTAL XRD STUDY OF 4,4'-DIPYRIDYL —
p-ETHOXYBENZOIC ACID AND N,N'-DIPYRIDYLPYPERAZINE —
p-ETHOXYBENZOIC ACID CO-CRYSTALS:
DIRECT EVIDENCE OF H-BOND INTERACTION
IN THE CORRESPONDING LIQUID-CRYSTALLINE
MESOGENIC PHASES**

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Supramolecular H-bonded complexes formed between *p*-ethoxybenzoic acid and 4,4'-dipyridyl or N,N'-dipyridylpiperazine were obtained as nematic liquid-crystalline phases. The corresponding crystals suitable for single crystal X-ray analysis were isolated and investigated. The stoichiometry of complex **1** is (4,4'-dipyridyl)-2(*p*-ethoxybenzoic acid) and that of complex **2** is (N,N'-dipyridylpiperazine)-2(*p*-ethoxybenzoic acid). The molecular packing observed in the crystal structures investigated indicates that the mesogenic phases of the complexes are induced by H-bond interactions.

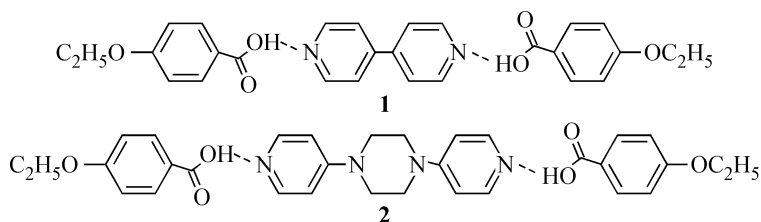
Keywords: bipyridine, molecular crystals, liquid crystals, nematic, mesogenic.

The preparation and characterization of supramolecular liquid crystals resulting from intermolecular H-bond interaction have been extensively studied over last 15 years, and several review articles have been published [1]. Particularly, after Kato and Frechet raised the concept for the construction of liquid crystalline compounds by the H-bond interaction between pyridine and acid derivatives [2], various types of such phases were prepared and investigated [3]. It is well known that molecular arrangement in the mesogenic phases of liquid crystals is closely related to the molecular packing in the crystalline state and thus investigation of the crystals by X-ray structure analysis directly provides information on the conformation and surroundings of the molecules. Although a great number of crystallographic analyses on such crystals have been conducted [4], studies on H-bond complexes of pyridine — acid combinations, to the best of our knowledge, are very limited [5].

Previous work on the identification of H-bonded liquid crystalline complexes were based on powder XRD and differential scanning calorimetry (DSC) methods, as good quality single crystals of the H-bonded complexes are not easy to prepare. This difficulty may arise from the weak interaction of pyridine (H-bond acceptor) and benzoic acid (H-bond donor) derivatives. According to the literature, the complexes **1** and **2** do form nematic phases during the thermal processes [3, 5]. In this work we isolated good quality crystals of the complexes **1** and **2** and studied them by single crystal X-ray analysis.

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Experimental. Preparation of complexes 1 and 2. 4,4'-Dipyridyl was from ACROS and N,N'-dipyridylpiperazine was prepared according to the literature [5, 6]. 4,4'-dipyridyl (0.16 g, 1 mmol) and *p*-ethoxybenzoic acid (0.34 g, 2 mmol) were dissolved in THF (20 ml); the resulting solution was left for one week to evaporate. Crystals of complex **1** were filtered off, washed with anhydrous ether and dried. Crystals of complex **2** were prepared similarly.

X-ray crystallography. Single crystals of **1** (0.20×0.15×0.10 mm) and **2** (0.43×0.41×0.36 mm) of suitable quality, obtained as described above, were mounted on glass fibers and studied.

Complex **1** was studied on a Nonius Kappa CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 295 K. The θ range for data collection was 1.86–27.49°. No significant decay was observed during the data collection. Collected reflections 15,586; used 10,918; observed ($I \geq 2\sigma(I)$) 5465. Data were processed on a PC using SHELXTL software package [7]. The structure of **1** was solved using direct methods and refined by full-matrix least squares on F^2 values. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were identified by calculation. The final indices (observed data) were $R = 0.0581$, $wR2 = 0.1452$ with *GOOF* on F^2 of 1.059.

According to the analysis, the gross formula of **1** is C₂₈H₂₈N₂O₆; formula weight 488.52; the crystal was monoclinic, space group $P2_1$, $a = 9.2046(2) \text{ \AA}$, $b = 21.1011(6) \text{ \AA}$, $c = 13.1030(3) \text{ \AA}$, $\beta = 101.265(1)^\circ$, $V = 2495.93(11) \text{ \AA}^3$, $Z = 4$; calculated density 1.300 g/cm³.

Complex **2** was studied on a Bruker Smart CCD diffractometer with graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The θ range for data collection was 2.84–25.97°. No significant decay was observed during the data collection. Collected reflections 7931; used 3836; observed ($I \geq 2\sigma(I)$) 3049. Data were processed on a PC using SHELXTL software package [7]. The structure of **2** was solved using direct methods and refined by full-matrix least square on F^2 values. All non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were identified by calculation. The final indices (observed data) were $R = 0.0439$, $wR2 = 0.1380$ with *GOOF* on F^2 of 1.002.

According to the analysis, the gross formula of **2** is C₃₂H₃₆N₄O₆; formula weight 572.65; the crystal is monoclinic, space group Pc , $a = 13.241(2) \text{ \AA}$, $b = 8.805(1) \text{ \AA}$, $c = 13.531(2) \text{ \AA}$, $\beta = 113.556(2)^\circ$, $V = 1446.1(3) \text{ \AA}^3$, $Z = 2$; calculated density 1.315 g/cm³.

Full crystallographic data for complexes **1** and **2** have been deposited with Cambridge Crystallographic Data Center as supplementary publications CCDC-270189 and CCDC-259670, respectively. Copies of the data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.cam.ac.uk) or at www.ccdc.cam.ac.uk/data_request.cif.

Results and discussion. According to the literature, 4,4'-dipyridyl, N,N'-dipyridylpiperazine and *p*-ethoxybenzoic acid do not form any mesogenic phases themselves, but their complexes **1** and **2** show a nematic phase in the range of 150–169 and 202–205°C, respectively, in the course of a thermal process [3, 5]. As a result of this study, the complexes **1** and **2** also exist as regular molecular crystals (co-crystals) with 1:2 molar ratio of dipyrindyl and acid molecules.

A fragment of the crystal structure of complex **1** is shown in Figure 1. Clearly, the H-bond interaction significantly influences the arrangement of molecules in the crystal. There are two independent molecules of 4,4'-dipyridyl and four independent molecules of *p*-ethoxybenzoic acid in the structure (Fig. 1). They form two three-molecule associates. Four H-bonds between OH and N of adjacent molecules form, with H1...N1, H1'...N1', H2...N2 and H2'...N2' being 1.920, 1.713 Å, 1.880 Å, and 1.683 Å, respectively. The distances are shorter than the corresponding sums of van der Walls radii

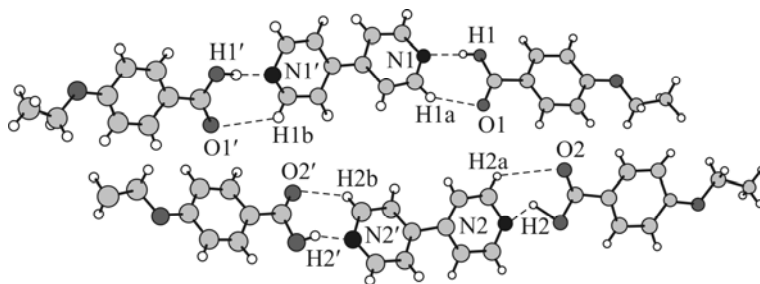


Fig. 1. The H-bond interactions in the two independent associates in the crystal structure of complex **1**.

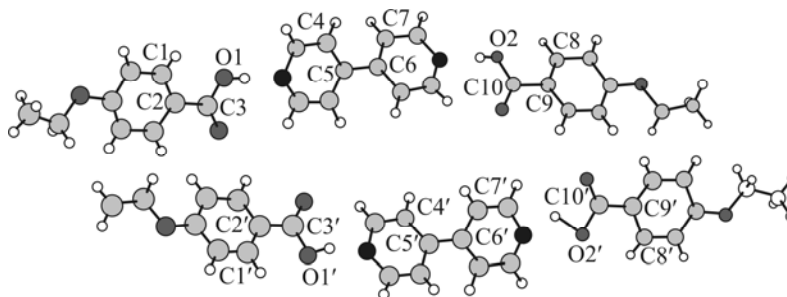


Fig. 2. Complex **1** (the same fragment as in Figure 1). Atom numbering to show the dihedral angles between molecular fragments.

of H and N atoms (Bondi radii: H 1.20 Å, N 1.55 Å [8a]) and fall in the range of usually observed for strong H-bonds. Additionally, four H-bonds between CH and O of adjacent molecules were observed, with H1a...O1, H1b...O1', H2a...O2 and H2b...O2' being 2.617 Å, 3.037 Å, 3.047 Å, and 2.633 Å, respectively. The distances are close to the corresponding sums of van der Waals radii of H and O atoms (Bondi radii: H 1.20 Å, O 1.52 Å [8a]) indicating weak interactions. Finally, weak H-bond interactions between molecules of adjacent associates are observed, in the 2.441–2.890 Å range. Noteworthy, the C_{sp^3} -H or C_{sp^2} -H in this case acts as an H-bond donor for the formation of intermolecular H-bond with O atom in the crystal framework. Similar interactions were observed in other systems [8b–8d]. Although some of these interactions are not strong, however, according to Desiraju and co-workers, these O...H distances are still in the range of a weak hydrogen bond [8e].

As mentioned above, the primary and secondary H-bonds in the structure of complex **1** form a three-dimensional network. The two pyridyl rings are 29° to each other. The dihedral angles C4–C5–C6–C7 and C4'–C5'–C6'–C7' in the two dipyridyl molecules are 29.75° and 29.72°, respectively. The dihedral angles of C1–C2–C3–O1, C8–C9–C10–O2, C1'–C2'–C3'–O1' and C8'–C9'–C10'–O2' in the four independent ethoxybenzoic acid molecules are 0.60°, 10.91°, 8.31°, and 4.73°, respectively (Fig. 2). These observations are quite unusual and may arise from the 3D H-bond interactions. In addition to the H-bond interactions, the quadrupolar interaction between intermolecular benzene moieties also is significant in molecular stacking [4]. The aryl H atoms of the ethoxybenzoic acid are directed to the plane containing dipyridyl moiety and the angle between the planes containing benzene moieties of the molecules was estimated to be about 30°.

A fragment of the crystal structure of complex **2** is shown in Fig. 3. Strong H-bonds exist between OH group of the acid and N atom of the pyridine moiety. The corresponding distances of H1...N1 and H1'...N1' are 1.77 Å and 1.78 Å, respectively, shorter than the corresponding sums of van der Waals radii of H and N atoms. Interestingly, the average H-bond distance H...N in complex **2** is 1.775 Å, which is slightly shorter than that of H...N in complex **1** (1.799 Å). This may arise from the stronger lone-lair donating ability of the N(ring) in N,N'-dipyridylpiperazine. Also, intermolecular H-bonds are observed with O1...H2 and O1'...H2' distances of 3.05 Å and 2.99 Å, respectively, which are slightly longer than the sum of the van der Waals radii of H and O atoms. These O...H distances are still in the range of a weak hydrogen bond [8b].

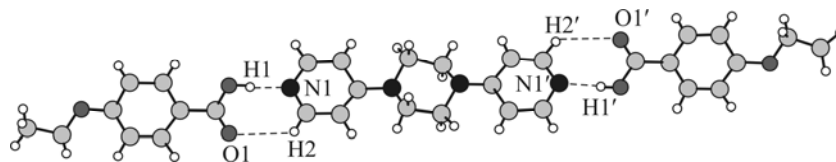


Fig. 3. The main H-bond interactions in the in the crystal structure of complex **2**.

Compared with the H-bond interaction between adjacent associates in complex **1**, the corresponding H-bond interaction in complex **2** is simpler.

The molecular alignment of associates in complexes **1** and **2** is parallel and one-dimensional. This arrangement is very similar to molecular packing characteristic of the nematic phase, and that may be the reason why complexes **1** and **2** form a nematic phase directly from the solid state during the heating process.

In summary, crystals suitable for single crystal structure determination were obtained from *p*-ethoxybenzoic acid and either 4,4'-dipyridyl or dipyridylpiperazine, both with 2:1 molar ratio. The secondary H-bond interactions form a three-dimensional network in complex **1** and two-dimensional network in complex **2**. Various types of H-bond interactions were observed.

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