

Cocrystal Structure of the Redox-active Phenylenediamine and Quinonediimine Derivatives

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The cocrystal structure of diethyl 2,5-bis{[4-(ethoxycarbonyl)phenyl]amino}terephthalate (PDA) and diethyl (3*E*,6*E*)-3,6-bis{[4-(ethoxycarbonyl)phenyl]amino}cyclohexa-1,4-diene-1,4-dicarboxylate (QDI) was determined by X-ray crystallography. The compound crystallizes in a triclinic system and was characterized thus: *P*-1, *a* = 8.6778(3) Å, *b* = 13.0702(4) Å, *c* = 13.5152(4) Å, α = 79.1570(15)°, β = 71.8459(15)°, γ = 72.5962(16)°, *Z* = 1, *V* = 1382.28(7) Å³. The *R*1 [*I* > 2σ(*I*)] and *wR*2 (all data) values are 0.078 and 0.190, respectively, for all 4179 independent reflections. In the crystal, a polymeric alternating arrangement of PDA and QDI exists through a network of π-π interactions, wherein both components adopt an *anti*-conformation of the π-conjugated backbones.

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π-Conjugated organic molecules and polymers are promising candidates for a variety of applications, including flexible electrodes,¹ light-emitting diodes,² field-effect transistors³ and so on. Control of the redox properties of π-conjugated moieties can be used for further functionalization. Polyanilines is unique among the most common classes of conductive organic polymers and is used in many fields.^{4,5} Polyanilines consist of three different redox forms: fully reduced leucoemeraldine, semi-oxidized emeraldine and fully oxidized pernigaline base forms. Oligoanilines are used as model compounds of polyaniline, due to good solubility, well-defined structures and similar redox properties. Thereby, a series of oligoanilines have been synthesized and characterized.⁶⁻⁸ 1,4-Phenylenediamine and 1,4-quinonediimine are reduced and oxidized π-conjugated units of polyanilines, respectively.⁹ We previously demonstrated the redox switching of the emission properties of Ru(II) dipyriddy complexes bearing 1,4-phenylenediamine moieties by changing the redox states of the 1,4-phenylenediamine moieties.¹⁰⁻¹² Moreover, switching and tuning of the luminescent properties of 2,5-bis(arylamino)terephthalate derivatives were also achieved.¹³⁻¹⁵ We herein report on a structural determination of cocrystal composed of diethyl 2,5-bis{[4-(ethoxycarbonyl)phenyl]amino}terephthalate (PDA) and diethyl (3*E*,6*E*)-3,6-bis{[4-(ethoxycarbonyl)phenyl]amino}cyclohexa-1,4-diene-1,4-

dicarboxylate (QDI) (Fig. 1).

In this research, the synthetic procedures of PDA and QDI have been already reported and fully characterized.¹³ The titled cocrystal was obtained by slow-evaporation of a solution of pure QDI in acetone under an air atmosphere. A red block crystal of suitable size was mounted on a grass fiber and all measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite-monochromated Cu Kα (λ = 1.54187 Å) radiation.¹⁶ The structure was solved by SIR2004,¹⁷ SHELXL Ver. 2018/3¹⁸ and CrystalStructure Ver. 4.3 program.¹⁹ The refinement was carried out by using full-matrix least squares on *F*². H atoms involved in hydrogen-bonding interactions were located in difference electron-density maps and were fully refined. Crystal data, data collection, and structure refinement details are summarized in Table 1, selected bond lengths (Å) and angles (°) are listed in Table 2. The hydrogen-bonding geometry and

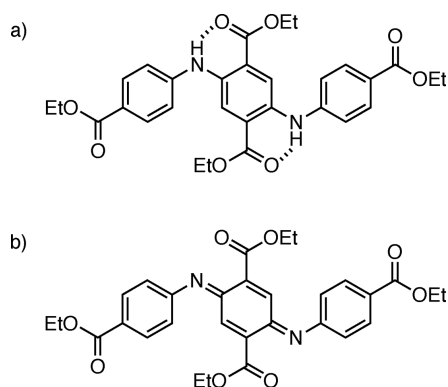


Fig. 1 (a) PDA and (b) QDI. Intramolecular hydrogen bonds are shown by the dotted line.

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Table 1 Crystal and experimental data

Chemical formula: C ₆₀ H ₆₂ N ₄ O ₁₆	
Formula weight = 1095.13	
T = 173 K	
Crystal system: triclinic	Space group: <i>P</i> -1
<i>a</i> = 8.6778(3) Å	α = 79.1570(15)°
<i>b</i> = 13.0702(4) Å	β = 71.8459(15)°
<i>c</i> = 13.5152(4) Å	γ = 72.5962(16)°
<i>V</i> = 1382.28(7) Å ³	<i>Z</i> = 1
<i>D</i> _x = 1.316 g/cm ³	
Radiation: Cu <i>K</i> α (λ = 1.54187 Å)	
μ (Cu <i>K</i> α) = 0.80 mm ⁻¹	<i>F</i> (0 0 0) = 578
Crystal size = 0.70 × 0.60 × 0.20 mm ³	
No. of reflections collected = 14348	
No. of independent reflections = 4179	
θ range for data collection: 5.78 to 62.52°	
Data/Restraints/Parameters = 4179/18/366	
Goodness-of-fit on <i>F</i> ² = 1.06	
<i>R</i> indices [<i>I</i> > 2σ(<i>I</i>):] <i>R</i> 1 = 0.063, <i>wR</i> 2 = 0.171	
<i>R</i> indices (all data): <i>R</i> 1 = 0.078, <i>wR</i> 2 = 0.190	
Δ (σ) _{max} < 0.001	
$\Delta\rho$ _{max} = 0.69 eÅ ⁻³	$\Delta\rho$ _{min} = -0.52 eÅ ⁻³
Measurement: Rigaku R-AXIS RAPID diffractometer	
Program system: RAPID AUTO	
Structure solving program: Direct methods (Sir2004)	
Structure determination: SHELXL 2018/3	
Refinement: Full-matrix least-squares on <i>F</i> ²	
CCDC deposition number: 1834237	

Table 2 Selected bond lengths (Å) and angles (°)

C2-C3*	1.389(4)	C1-N1-C4	127.4(2)
C22-C23	1.342(4)	C21-N2-C24	120.9(2)
C1-N1	1.394(3)		
C21-N2	1.289(4)		

Symmetry operators: *, -*x*, -*y*+1, -*z*+1.

selected dihedral angles between least-squares planes are given in Tables S1 and S2, respectively.

A perspective view of the obtained structure is shown in Fig. 2. The cocrystal has a 1:1 molar ratio of PDA and QDI, as shown. Therefore, some QDI might undergo a reduction to PDA under the conditions under which the cocrystal was obtained. The molecular structures of each component, PDA and QDI, and atomic numbering scheme are shown in Fig. 3. Both component molecules were found to form *anti*-conformations of the π -conjugated moieties. In PDA component, intramolecular hydrogen bonds between the amino hydrogen of the phenylenediamine moiety and the carbonyl oxygen of the ethoxycarbonyl group at the central benzene ring were formed to induce *anti*-conformations of the π -conjugated phenylenediamine backbone (Fig. 3a). The terminal and central benzene rings are oriented with a dihedral angle of 47.4(1)° (Table S2). This is probably due to a steric repulsion between the *ortho*-hydrogen atoms, despite the formation of intramolecular hydrogen bonds, which might induce a coplanar structure of the π -conjugated moiety. On the other hand, the QDI component has dihedral angles of 68.5(1)° between the terminal and central benzene rings, as shown in Fig. 3b and Table S2. This value is larger than that of the PDA component. The short imine bond length of QDI (1.29 Å, Table 2) might cause a greater steric repulsion between the *ortho*-hydrogen atoms at the central and

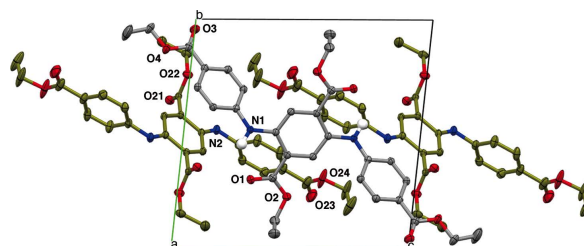


Fig. 2 View showing the crystal packing (gray, PDA; gold, QDI) down the *a*-axis. Displacement ellipsoids are drawn at the 30% probability level. C-bound H atoms are omitted for clarity.

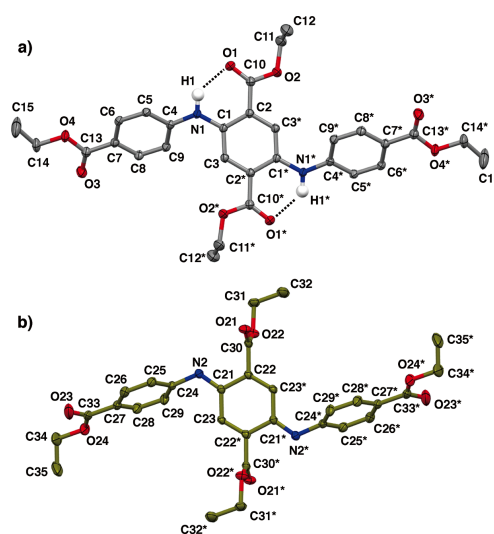


Fig. 3 Molecular structures of the (a) PDA and (b) QDI components, showing the atom-labelling scheme and the hydrogen bonds within the selected asymmetric unit (dashed lines). Displacement ellipsoids are drawn at the 30% probability level and the atoms marked with an asterisk (*) are at the symmetry position (a) (-*x*, -*y*+1, -*z*+1) and (b) (-*x*+1, -*y*+1, -*z*). C-bound H atoms are omitted for clarity.

terminal benzene rings. The π - π interactions between the benzene rings of each component were observed, wherein central benzene ring (C21-C22-C23-C21*-C22*-C23*) of QDI was sandwiched between two terminal benzene rings (C4-C5-C6-C7-C8-C9) of PDA (Fig. S1). The dihedral angle between the central benzene ring (C21-C22-C23-C21*-C22*-C23*) of QDI and the terminal benzene rings (C4-C5-C6-C7-C8-C9) of PDA was 17.2(2)° with a distance of 3.72 Å between their mean planes (Table S2). A polymeric alternating arrangement of PDA and QDI appeared to be stabilized through intermolecular interactions.

In conclusion, structural characterization of the cocrystal of diethyl 2,5-bis{[4-(ethoxycarbonyl)phenyl]amino}terephthalate (PDA) and diethyl (3*E*,6*E*)-3,6-bis{[4-(ethoxycarbonyl)phenyl]amino}cyclohexa-1,4-diene-1,4-dicarboxylate (QDI), which is an example of the cocrystal of the reduced and oxidized forms of π -conjugated units of polyanilines, was demonstrated. The single-crystal X-ray structure determination of the cocrystal reveals a polymeric alternating arrangement of PDA and QDI through a network of π - π interactions, wherein both components

adopt an *anti*-conformation of the π -conjugated backbones. The PDA component was found to form intramolecular hydrogen bonds between the amino hydrogen and carbonyl oxygen to induce the *anti*-conformation of the π -conjugated phenylenediamine backbone.

Supporting Information

This material is available free of charge on the Web at <http://www.jsac.or.jp/xraystruct/>.

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