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Synthesis and crystal structure of 3-(4'-nitrophenyl)iminocoumarin, and cylization reaction mechanism based on DFT calculation

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Abstract

A convenient method was reported to synthesize $3 \cdot (4'-nitrophenyl)$ iminocoumarin by a cyclization reaction following a Knoevenagel reaction of 2-hydroxybenzaldehyde with 4-nitrophenylacenitrile in an ethanol solution. Piperidine or piperazine was employed respectively as catalyst. Crystal structure of $3 \cdot (4'-nitrophenyl)$ iminocoumarin shows that the molecules are H-aggregation due to π - π stacking and hydrogen bonds between adjacent molecules, as a result, electrons would transfer easily from a molecule to an adjacent molecule. Based on theoretical calculations of the electronic structures and thermodynamic parameters of the reactive intermediates in these cyclization reactions, the reaction mechanisms were postulated. Data of single crystal and spectrum of UV-vis absorption show that $3 \cdot (4'-nitrophenyl)$ iminocoumarin is good π -conjugated compound and would be potentially employed as donor-acceptor polymer units for developing bulk heterojunction solar cell. This paper suggests a convenient and effective method for synthesizing ring-locked D-A copolymer units for developing solar cell materials.

Keywords: Crystal structure; Cyclization reaction; DFT calculation; Reaction mechanism; Iminocoumarin; Bulk heterojunction solar cell.

Introduction

Opto-electronic properties of compounds usually depend on its geometric structure. [1-3] Syntheses of organic or polymeric compounds with desired geometric structures is a fatal procedure for developing bulk heterojunction (BHJ) solar cells with high power change efficient (PCE).[2-6] Generally, a desired organic compound or donor-acceptor (D-A) copolymer unit should be π -conjugated well in order that donor materials would exhibit high mobility, because π -conjugated compounds usually aggregate to ordered structure in quenching procedure of making solar cell due to π - π stacking and hydrogen bonds.[4-8] Suzuki reaction and Stille reaction were developed for syntheses of π -conjugated copolymer containing D-A units.[9-10] However, the reaction systems must be oxygen free. Catalysts of these reactions are expensive so that synthesized polymers are too expensive to be industrialized for developing organic solar cell devices. Therefore, it would be interesting that a convenient and effective method would be developed to synthesize copolymer containing D-A units.[1,11-12] Knoevenagel reaction is high performance for forming double bond C=C under a convenient condition.[13-14] A compound containing two aryl rings connected with a double bond C=C isn't *π*-conjugated well. However, a compound containing two aryl rings connected with a ring-locked double bond C=C is usually π -conjugated well.[15-16] Therefore, it is useful that a ring-locked reaction would take place following a Knoevenagel reaction of an aryl compound containing electron-withdrawing substitute group with compound containing electron-pushing substitute an aryl group.

4-Nitrophenylacenitrile reacted with 2-hydroxylbenzaldehyde in an ethanol solution to acquire 3-(4'-nitrophenyl)iminocoumarin. The designed compound is a well π -conjugated molecule so that it could be employed as D-A copolymer units for developing organic solar cell. Organic solar cell materials containing this kind of polymer units could exhibit a good mobility, because the π electrons would be better delocalized in the whole molecule.[17-18] Synthetic method of iminocoumarin derivatives was seldom researched.[19-20] Complex synthetic method that resin was used as catalyst and polymeric solid support results that the product was too expensive to be widely used as an opto-electron materials. Therefore, it is of great interest that a convenient and environmentally benign method would be developed to synthesize the compound. In this paper, 3-(4'-nitrophenyl)iminocoumarin was synthesized by a cyclization reaction following a Knoevenagel reaction of 2-hydroxybenzaldehyde with 4-nitrophenylacenitrile in an ethanol solution. Its crystal structure was determination by X-ray analysis.[21] The reaction mechanism was supposed based on time dependent density functional theory (TD-DFT) calculations of the electronic structures and thermodynamic parameters of the reaction intermediates at the B3LYP/6-31G(d) level.[22-23]. It would suggest a convenient and effective method for synthesizing polymers containing ring-locked D-A units, similar to 3-(4'-nitrophenyl)iminocoumarin, used as organic solar cell materials.

Results and discussion

1. Synthetic method and catalysis activity

3-(4'-Nitrophenyl)iminocoumarin was synthesized by a cyclization reaction following a Knoevenagel reaction of 2-hydroxybenzaldehyde with 4-nitrophenylacenitrile in an ethanol

solution. Piperidine or piperazine was employed respectively as catalyst. Acetic acid was used to control pH value of reaction solution in the range from 9 to 11. A dehydration agent, anhydrous Na₂SO₄, was added into the reactive solution to remove water given from cyclization reaction for improving yield of 3-(4'-nitrophenyl)iminocoumarin. The reactions were shown in **Scheme 1**.



Scheme 1. Sythesis of 3-(4'-nitrophenyl)iminocoumarin.

Scheme 1 shows that the yields of 3-(4'-nitrophenyl)iminocoumarin were 84.2% and 92.5 % when piperidine or piperazine was employed as a catalyst, respectively. Piperazine is a better catalyst than piperidine due to nucleophilicity of lone pair electrons.



Scheme 2. The structure of piperazine or piperidine optimized by DFT calculations and atomic

charges (unit: atomic unit) of N atoms.

The structures of piperazine and piperidine were optimized by TD-DFT calculations using Gaussian03 software at the B3LYP/6-31G(d) level.[22-23] Nucleophilicity of lone pair electrons in piperazine was stronger than that of piperidine because negative charge (Mulliken atomic charges: -0.555 A.U.) of nitrogen atom in piperazine was denser than that (Mulliken atomic charges: -0.545 A.U.) in piperidine. [13-14] Carbon atom in the carbonyl group would be attacked

more easily by nitrogen atom in piperazine to form 2-hydroxybenzaldehyde dipiperazine acetal.[13-14] Therefore, piperazine was a better catalyst than piperidine. Using piperazine as catalyst, the yield is higher.

2. Mechanism of reaction

Density Functional Theory (DFT) calculation at B3LYP/6-31G (d) have been used to suggest reaction mechanism.[24-25] The suggested mechanisms have well predicted experimental results.[24-25] Therefore, based on TD-DFT calculations on the electronic structures and thermodynamic parameters of the reaction intermediates and resultants in the cyclization reaction, the mechanisms of the reactions were postulated.[22-23]



Scheme 3. Mechanism of the cyclization reaction.

The mechanism was proposed for the reactions of 4-nitrophenylacenitrile with 2-hydroxybenzaldehyde to acquire 3-(4'-nitrophenyl)iminocoumarin in an ethanol solution of alkaloid. (Scheme 3) At first, there was a Knoevenagel reaction of 4-nitrophenylacenitrile with 2-hydroxybenzaldehyde to acquire intermediate 1. The hydroxyl in intermediate 1 was deprotonated to give a phenolic anion derivative (2) in an ethanol solution of alkaloid. Charge of the phenolic anion in intermediate 2 transferred to carbon atom of nitrile to form a single bond O-C. Charge of triple bond of nitrile group transferred to nitrogen atom of nitrile group to form a double bond C=N, at the same time, a proton was seized by nitrogen atom of nitrile to form a

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single bond N-H. As a result, 3-(4'-nitrophenyl)iminocoumarin was synthesized.

Enthalpies, entropies, energies and free energies of reactants, resultants and intermediates are

summarized in Table 1.

Table 1. Thermodynamic parameters of reactants, resultants and intermediates (Unit: KJ/mol),

No.	Comp.	H^{a}	S^{a}	E^{a}	G ^a ΔG
					h
1	Resultant	-2395349.9	0.5035	-2395352.4	-2395500.1 -76.0°
2	2-Hydroxybenzaldehyde	-1104130.7	0.3428	-1104133.2	-1104232.9
3	4-Nitrophenylacenitrile	-1491362.7	0.3776	-1491365.1	-1491475.3
4	Water	-199811.1	0.1896	-199813.6	-199867.6
5	3-(2-Hydroxyphenyl)-2-	-2395268.9	0.5204	-2395271.4	-2395424.1 -416.5^{c}
	(4-nitrophenyl)acrylonitrile				

^a H, S, E and G are sum of electronic and thermal enthalpies, entropies, energies and free energies.

^b Change of free energy in procedure from compound 5 to compound 1 is calculated by following equation, $\Delta G_1 = G_1 - G_5 = (H_1 - H_5) - T(S_1 - S_5)$

^c Change of free energy in the reaction of compound 2 with compound 3 to produce compound 5 is calculated by following equation, $\Delta G_5 = (G_5 + G_4) - (G_2 + G_3) = (H_5 + H_4 - H_2 - H_3) - T(S_5 + G_5) - T(S_5 + G_$ $S_4 - S_2 - S_3$).

In Table 1, ΔG_5 (- 416.5 KJ/mol) is a big negative value in 298.15 K, therefore, 2-hydroxybenzaldehyde would react completely with 4-nitrophenylacenitrile to produce 3-(2-hydroxyphenyl)-2-(4-nitrophenyl)acrylonitrile. In the reaction procedure, change of enthalpy - 413.4 KJ/mol. Moreover, change of entropy is -0.0104 KJ/mol. Therefore, the reaction would carry on spontaneously. In 298.15 K, ΔG_1 (-76 KJ/mol) is also a big negative value, therefore, 3-(2-hydroxyphenyl)-2-(4-nitrophenyl)acrylonitrile would change to title compound. In the procedure, change of enthalpy is - 81 KJ/mol. Moreover, change of entropy (- 0.0169 KJ/mol) is very small. Therefore, the reaction would carry on spontaneously. In addition, the energy of

compound 5 (-2395271.4 KJ/mol) is higher than that of compound 1 (-2395352.4 KJ/mol). It suggests that compound 5 trends to transfer to compound 1.

3. Computational details

The cyclization reaction mechanism was suggested based on theoretical calculation of the reaction intermediates. Geometries were optimized by TD-DFT calculations using Gaussian03 software at the B3LYP/6-31G(d) level.[22-23] All results support the suggested mechanism. The

results of the calculations are shown as following.



Figure 1. The structure of intermediate 1 optimized by TD-DFT and atomic charges (unit:

atomic unit).

Figure 1 shows clearly that H30 (Positive charge: 0.420 A.U.) was attacked easily by

electron doublet of nitrogen atom at alkaloid to give the deprotonated intermediate 2.



Figure 2. The structure of intermediate 2 optimized by DFT calculations and atomic charges

(unit: atomic unit).

Figure 2 shows that negative charge delocalization from the O⁻ in the intermediates **2** to the carbon atom in nitrile group results the bond between O28 and C13. Charge of triple bond of nitrile group transferred to N29, at the same time, N29 was attacked easily by proton to give 3-(4'-nitrophenyl)iminocoumarin.



Figure 3. The structure of intermediate 3 optimized by DFT calculations, atomic charges and bond length between C13 and O27 (unit: atomic unit).

Charge of O28, N29, C13 and H30 are -0.513, -0.605, 0.451 and 0.298 (Unit: A.U.). Length of bond between C13 and O28 being 1.386 Å shows that the bond is a normal singer bond. The length of bond (1.26 Å) between C13 and N25 is a double bond.

4. Crystal structure

The geometry of title compound was studied by summarizing crystallographic data.[21] Part A of Figure 4 shows that the molecule is π -conjugated well because pyran ring and benzene ring (C1-C2-C3-C4-C5-C9) are coplanar. Nitro group is in a plane of benzene ring containing C10. Part B of Figure 4 shows clearly that title molecules are H-aggregation through π - π stacking. This organic crystalline materials exhibits a short interplanar distance (3.493 Å). As a result, π -electrons would transfer easily from a molecule to an adjacent molecule in the lamellar π - π stacked structural materials.[26-30] Therefore, the planar compounds are significant for many applications. Hydrogen bond was formed between a hydrogen atom of hydroxyl group and an

oxygen atom of nitro group at an adjacent molecule. Hydrogen bond was also formed between a hydrogen atom of nitrobenzene ring and an oxygen atom of pyran ring at an adjacent molecule (Part B of Figure 4). These hydrogen bonds and π - π stacking affections result that the title compounds were stacked up to crystal, which is useful property for developing BHJ solar cell with high PCE. [8, 31-35]



Figure 4. Crystal of 3-(4'-nitrophenyl)iminocoumarin (Part A: Structure geometry of a molecule

3-(4'-nitrophenyl)iminocoumarin. Part B: The crystal structures viewed along the a-axis. Part C:

The crystal structures viewed along the b-axis.).

Table 2 Crystal data and summary of structure refinement for title compound.

CCDC deposit no.	982576
Empirical formula	$C_{15}H_{10}N_2O_3$
Formula weight	266.25
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, $P2(1)2(1)2(1)$
Unit cell dimensions	a = 3.7837 Å alpha = 90 deg.
	b = 14.7712 Å beta = 90 deg.
	c = 21.858 Å gamma = 90 deg.

Volume	1221.6(3) Å ³
Z, Calculated density	4, 1448 Kg/m ³
Absorption coefficient	0.103 mm^{-1}
F(000)	552
Crystal size	0.40 x 0.38 x 0.34 mm
Theta range for data collection	2.754 to 22.783 deg.
	-4<=h<=4, -17<=k<=17,
Limiting indices	-26<=1<=23
Reflections collected / unique	8703 / 2171 [R(int) = 0.0347]
Completeness to theta = 25.01	99.7 %
Absorption correction	Multi-sacn
Max. and min. transmission	0.9657 and 0.9599
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2171/0/181
Goodness-of-fit on F ²	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0388, wR2 = 0.0855
R indices (all data)	R1 = 0.0570, wR2 = 0.0971
Largest diff. peak and hole	0.111 and -0.159 e. Å ⁻³

Table 2 shows that single crystal is orthorhombic crystal system, P2(1) 2(1) 2(1) space group.

The molecules aggregated face to face to form a big single crystal (0.40 x 0.38 x 0.34 mm) due to

 π -conjugated structure of molecule and the π - π stacking affection.

		Interatom	ic distance (Å)	Dihedral angle (°)		
	N1-C6	1.256(3)	C6-C7	1.468(3)	C6-O1-C9-C1	179.1(2)	
	C7-C8	1.340(3)	C5-C8	1.439(3)	N1-C6-C7-C8	178.0(2)	
	C5-C9	1.385(3)	C2-C3	1.390(3)	C4-C5-C8-C7	179.5(2)	
	C7-C15	1.484(3)	N2-C12	1.463(3)	C8-C7-C15-C10	132.6(2)	
	O1-C6	1.383(2)	O1-C9	1.387(2)	O2-N2-C12-C13	178.7(2)	
77	N1-H1	0.8600	C10-H10	0.9300	O3-N2-C12-C11	-178.8(2)	
	O3-N2	1.222(3)	O2-N2	1.218(3)	N1-C6-C7-C15	-2.1(4)	

Table 3. Selected interatomic distances and dihedral angles

Bond lengths of N1-C6, C7-C8, C5-C9, C2-C3 are 1.256 Å, 1.340 Å, 1.385 Å, 1.390 Å,

respectively. They are double bond. Bond lengths of single bonds C6-C7 (1.468 Å) and C5-C8 (1.439 Å) are shorter than that of C7-C15 (1.484 Å) due to π -electrons delocalized in pyran ring

O1-C6-C7-C8-C5-C9. Bond lengths of single bonds O1-C6 (1.383 Å) and O1-C9 (1.387 Å) are similar. Bond lengths of O3-N2 (1.222 Å) and O2-N2 (1.218 Å) are similar due to π -electrons delocalized in nitro group. Bond lengths of N1-H1 (0.860 Å) are shorter than that of C10-H10 (0.930 Å) because electronegativity of nitrogen atom are bigger than that of carbon atom. [36] Dihedral angle N1-C6-C7-C8 (178.0°) and C4-C5-C8-C7 (179.5°) show that pyran ring is in a plane. Dihedral angle C6-O1-C9-C1 (179.1°) shows that pyran ring and benzene ring C1-C2-C3-C4-C5-C9 are coplanar. Dihedral angle O2-N2-C12-C13 (178.7°) and O3-N2-C12-C11 (-178.8°) show that nitro group is in a plane of benzene ring C10-C11-C12-C13-C14-C15. Dihedral angle N1-C6-C7-C15 (-2.1°) shows atoms N1 and C15 are in a plane of the pyran ring. Dihedral angle C8-C7-C15-C10 (132.6°) shows that angle between C1-C2-C3-C4-C13-C14 plane and C10-C11-C12-C13-C14-C15 plane is 47.4° due to steric repulse between hydrogen atoms H14 and H8. If thiophene derivatives instead of benzene derivatives were used to synthesize benzopyran derivatives, designed compounds could be more suitable to be used as D-A copolymer units of donor materials for BHJ solar cell than title compound.



5. UV-vis absorption spectrum of 3-(4'-nitrophenyl)iminocoumarin

Figure 5. UV-vis absorption spectrum of title compound in CH_2Cl_2 (λ_{max} of the compound in

CH₂Cl₂ was marked on curves.).

UV-vis absorption spectrum of title compound in CH_2Cl_2 was determined by using a lambda 25 Perkin-Elmer spectrophotometer. Figure 5 shows that there are three absorption peaks in the UV-vis absorption spectrum. The solution of title compound in CH_2Cl_2 can effectively absorb light which wavelength is shorter than 400 nm. Therefore, UV-vis absorption spectrum shows that 3-(4'-nitrophenyl)iminocoumarin is good π -conjugated compound and would be suitable to be employed as D-A polymer units in donor materials of BHJ solar cells.[7, 18]

Conclusion

A conveniently method was reported to synthesize 3-(4'-nitrophenyl)iminocoumarin by a cyclization reaction following a Knoevenagel reaction of 2-hydroxybenzaldehyde with 4-nitrophenylacenitrile in an ethanol solution containing alkaloid in the pH range from 9 to 11. Piperidine or piperazine was employed respectively as catalyst. Anhydrous Na₂SO₄ was added into the reactive solution as a dehydration reagent. Crystal structure of 3-(4'-nitrophenyl)imino-coumarin shows that the molecules are H-aggregation due to π - π stacking and hydrogen bonds between adjacent molecules, as a result, electrons would transfer easily from a molecule to an adjacent molecule. Geometries, electronic structure, energies, enthalpies, entropies and free energies of reactants, resultants and intermediates were calculated using TD-DFT at the B3LYP/6-31G(d) level. Results of calculations show that title compound is a planar molecule and piperazine is a better catalyst. Based on results of theoretical calculations and experiments, the mechanisms of the cyclization reactions were postulated. Data of single crystal and spectrum of UV-vis absorption show that 3-(4'-nitrophenyl)iminocoumarin is good π -conjugated compound and would be potentially employed as D-A polymer units for developing BHJ solar cells. This

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paper would suggest a convenient and effective method for synthesizing polymer containing ring-locked D-A units, similar as 3-(4'-nitrophenyl)iminocoumarin, for developing BHJ solar cells with high PCE.

Experimental

Melting points were determined on a Yanaco micro melting point apparatus (uncorrected). ¹H NMR were recorded on Bruker AM 300 (Germany), and δ were given in ppm (relative to TMS) and coupling constants (*J*) in Hz. Mass spectra were recorded by a GCMS-QP2010 gas chromatogram mass spectrometer under GC/MS mode. UV-visible spectra were recorded on a Lambda 25 Perkin-Elmer spectrophotometer. IR spectra were recorded on a Brucker Vector 22 spectrophotometer, in which samples were embedded in KBr thin films. Precoated silica gel plates (GF254) were used for analytical TLC. All solvents were purified by standard procedures. All chemicals were purchased from Sigma or Aldrich.

3-(4'-Nitrophenyl)iminocoumarin was obtained as yellow crystal. The crystal structure was determined by Bruker CCD X-ray diffraction.[21] The analytical data of the compound (¹H NMR, ¹³C NMR, IR, MS) were in accord with the assigned structures, respectively.

Synthesis of 3-(4'-nitrophenyl)iminocoumarin. The 2-hydroxybenzaldehyde (2.44 g, 20.0 mmol), 4-nitrophenylacenitrile (4.14 g, 18 mmol) and anhydrous Na₂SO₄ (2.84g, 20 mmol) were added into anhydrous ethanol (50 mL) under a N₂ atmosphere. The mixture was heated, stirred and refluxed for 20 minutes. Then, the catalysts, piperidine (0.34g, 4 mmol) or piperazine (0.34g, 4 mmol) and acetic acid (0.12 g, 2 mmol), were added. A yellow precipitate was produced as soon as the catalyst was added. The reaction mixture was refluxed for 6 hours, cooled to room temperature. The reaction mixture was filtrated, washed by ethanol (20 mL \times 3) and dried to give

a yellow solid. The solid was recrystallized from acetnitril (25 mL) to give the pure compound 3-(4'-nitrophenyl)iminocoumarin as a yellow crystal (Piperazine used as catalyst: 4.43 g, 92.5 %; or Piperidine used as catalyst: 4.04 g, 84.2 %.).

¹H NMR (300 MHz, CDCl₃, 25°C, TMS) δ : 8.28 (d, ²J = 7.5 Hz, 2 H in nitrophenyl) ,7.87 (d,

 $^{2}J = 7.5$ Hz, 2 H in nitrophenyl), 7.70 (s, br, 1 H in imino), 7.60-7.40 (m, 2 H in benzopyran),

7.33 (s, 1 H in alkene), 7.22-7.05 (m, 2 H in benzopyran).

¹³C NMR (300 MHz, CDCl₃) δ: 115.49, 119.51, 123.58, 123.81, 128.42, 128.73, 129.78,

131.39, 132.59, 135.25, 142.97, 147.61, 153.49.

MS (⁺CESI) m/z: 267.42, calc. for C₁₅H₁₀N₂O₃ [M+1]⁺: 267.25.

UV-Vis (HCCl₃) λ_{max} : 352 nm (ϵ = 7605).

IR (KBr) v: 3370.7 (br, N-H) cm⁻¹, 1656.7 (C=N).[19-20]

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Highlight:

1. A convenient and novel cylization reaction for synthesizing

3-(4'-nitrophenyl)iminocoumarin is reported.

- 2. Its crystal structure shows that title molecules aggregate to lamellar π - π stacked structural materials.
- 3. The mechanisms of the cyclization reactions were postulated based on TD-DFT calculations.