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Substituted Benzoxazole and Catechol Cocrystals as an Adsorbent for CO_2 Capture: Synthesis and Mechanistic Studies

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KEYWORDS: CO_2 adsorption, Cocrystals, Substituted benzoxazole Synthesis, Mechanistic Studies, CO_2 adsorption capacity, Amine effect

ABSTRACT: We report the synthesis of cocrystals of a substituted benzoxazole and catechol from a primary amine and 3,5-di-*tert*-butylbenzoquinone. FT-IR and NMR spectroscopy studies revealed that cocrystals **2** could be synthesized in excellent yield from **1** and 3,5-di-*tert*-butylbenzoquinone. Introduction of an amine into the cocrystal structure enhanced the CO_2 adsorption capacity of the cocrystals at room temperature from 15.69 to 44.21 mg/g. Our results indicated the ability to use cocrystals for CO_2 capture and to easily modify them to enhance their CO_2 adsorption capacity.

Introduction

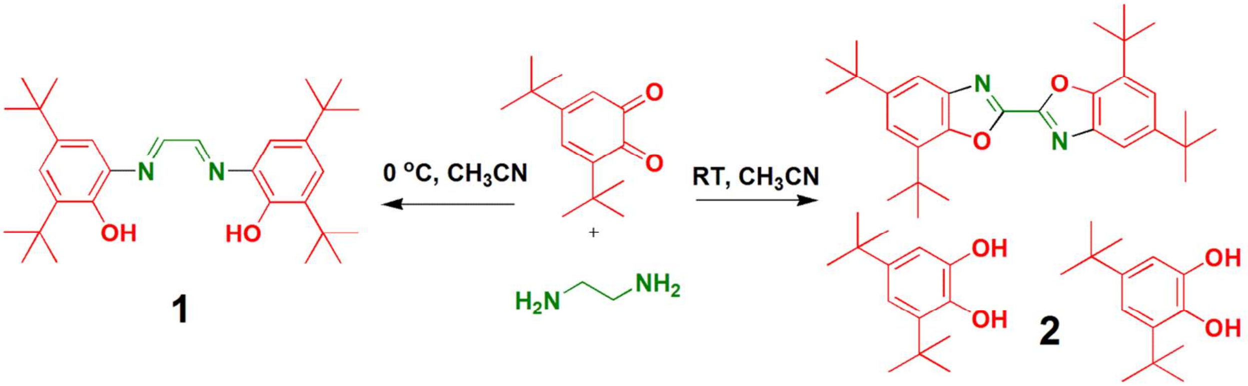
Globally, the ever-increasing concentration of CO_2 in the atmosphere due to the industrial effects of mankind is a widespread concern because of the undesirable effects of the resulting climate change that has been observed in recent years[1]. Various CO_2 capture technologies have been proposed to control the emission of this greenhouse gas in order to reduce the serious threat that it poses to ecosystems[3-12]. The adsorption method is preferred in carbon capture and storage (CCS)[13-16], and many adsorbents such as zeolites, metal organic frameworks (MOFs), amine-functionalized materials and activated carbon have been reported to capture CO_2[17-23]. Despite the many available adsorbents[24-26], it is vital to use the most suitable one to optimize the CO_2 separation efficiency in CCS. In this regard, few cocrystals that are able to adsorb CO_2 from a flue gas have been found. Cocrystals are defined as more than two types of molecules that form a crystalline solid and interact via non-covalent bonds[27,28]. Intermolecular interactions within the cocrystal define the molecular arrangement of the components in the solid state[29-32]. Due to their modularity, cocrystals have been used in solid-state organic synthesis, organic semiconductors and pharmaceutics[33,34]. In spite of their many achievements, cocrystals with amine functional groups have not been used for CO_2 adsorption studies in CO_2 capture processes. The adsorbents with amine functional groups have been very effective for CO_2 adsorption[8].

Herein we report the synthesis of cocrystals from the reaction of a primary amine with 3,5-di-*tert*-butylbenzoquinone. The cocrystals were characterized by using single-crystal X-ray analysis, FT-IR spectroscopy, NMR spectroscopy, and mass spectrometry. The CO_2 adsorption studies using these cocrystals were carried out at room temperature, and we analyzed the effect of incorporating an amine group into the cocrystal structure on the CO_2 adsorption.

Results and Discussion

Initially, a 1:2 ratio of ethylenediamine and 3,5-di-*tert*-butylbenzoquinone was stirred at 0 ^oC for 1 h to obtain **1** as a crystalline solid[35]. Stirring these reactants under the same conditions, except at room temperature for 12 h instead of at 0 °C for 1 h, unexpectedly afforded cocrystals of substituted benzoxazole and 3,5-di-tert-butylbenzene-1,2-diol, **2**, in a moderate yield of 12% (Scheme 1). **1** and the cocrystals were characterized by using ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy investigations as well as mass spectrometry. The imine protons of **1** appeared as a singlet at 8.82 ppm and aromatic protons appeared as a doublet with a $J_{\text{H-H}}$ coupling constant value of 2.2 Hz in the ^{1}H NMR spectrum; and the ^{13}C spectrum confirmed the presence of aromatic and aliphatic carbons (Figure S1). The ^{1}H and ^{13}C NMR spectra of **2** are shown in Figures S1 and S2. The absence of the imine proton peaks at 8.82 ppm in the ^{1}H NMR spectrum of **2** and the presence of aromatic proton peaks at 7.71 and 7.38 ppm with a $J_{\text{H-H}}$ coupling constant value of 1.7 Hz confirmed the presence of the benzoxazole ring in **2** (Figure S2).

The FT-IR spectrum of **1** showed a band at 3364 cm^{-1}, corresponding to hydroxyl group stretching vibrations, and a band at 1482 cm^{-1} which is corresponding to imine (-C=N) stretching vibrations. Bands at 3480 cm^{-1} and 3099 cm^{-1} were observed for **2**, and were attributed to two different types of hydrogen-bonds stretching vibrations, specifically -N…H-O and O-H…O, respectively, from 3,5-di-*tert*-butylcatechol and the substituted benzoxazole. Both **1** and **2** also yielded a band at 2953 cm^{-1} (Figure S3), corresponding to –CH stretching vibrations. To determine how the hydrogen bonding affected the nature of stretching vibrations in the cocrystals, FT-IR spectra were recorded for 3,5-di-*tert*-butylcatechol and 3,5-di-*tert*-butylbenzoquinone and are shown in Figure 4. Bands were observed at 1649 cm^{-1} and 3448 cm^{-1}, corresponding to –C=O stretching vibrations of benzoquinone and to the –OH group of 3,5-di-*tert*-butylcatechol, respectively.



Scheme 1. Syntheses of **1** and **2**

Light greenish crystals of **2** were obtained from CH_3CN and diethyl ether diffusion system. The crystal structure of **2** is shown in Figure 1 and the crystal information is given in Table S1 and S2. **2** crystallized in the triclinic system with space group P-1 and half a molecule per asymmetric unit. The distance between the N and C of benzoxazole ring was measured to be 1.2903(15) Å and that between C and O was 1.3588(13), values similar to the previously reported benzoxazole bond distances[36]. The bond distance between C and C1A of the benzoxazole dimer was measured to be 1.450 Å. **2** exhibits two types of intermolecular hydrogen bonds involving the catechol OH groups and benzoxazole N atoms. The catechol OH groups act as a donor in N···H-O interactions and as an acceptor in O-H···O interactions. These intermolecular hydrogen bonds are stabilizing the crystal structure. The distances between the acceptor and donor heteroatoms are 2.780 and 2.849 Å, and its respective angles are 141 and 164° (Table S3). These hydrogen bonds distances and angles suggest that in **2** strong hydrogen bonds are stabilizing the crystal system. Further the intermolecular N···H-O and O-H···O hydrogen bonds between benzoxazole and the catechol molecules are generating three-dimensional networks in **2** (Figure 2 & S4). Furthermore, to check the purity of cocrystals powder XRD data was collected and that was compared with simulated data (Figure S5). Measured XRD pattern of **2** was closely matched with those in the simulated pattern generated from single-crystal diffraction data; it indicates the formation of pure cocrystals.

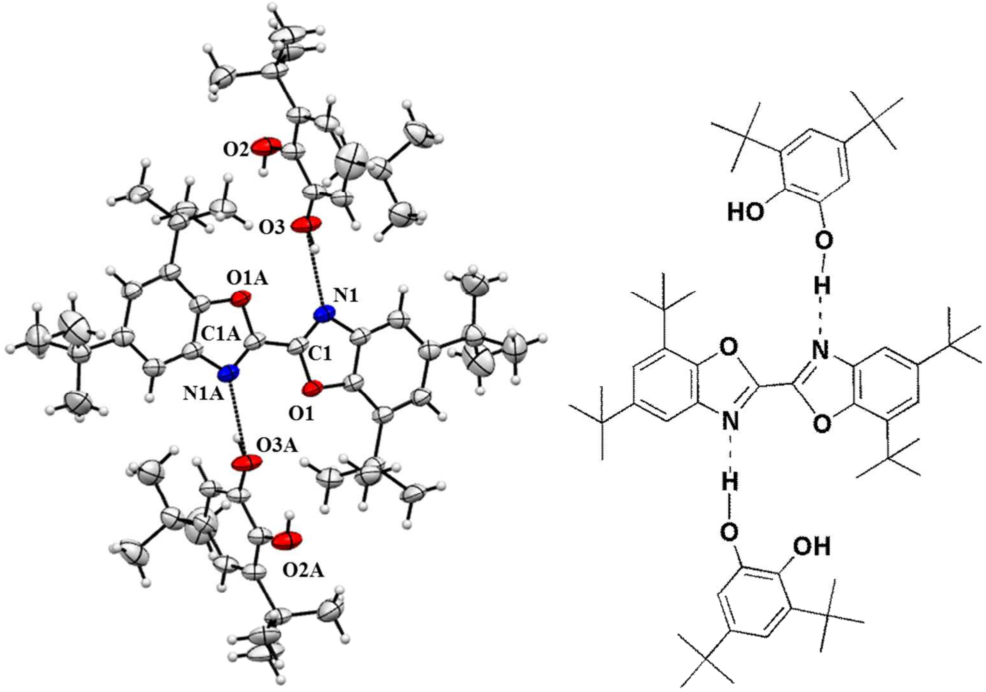


Figure 1. Single-crystal X-ray structure of **2**

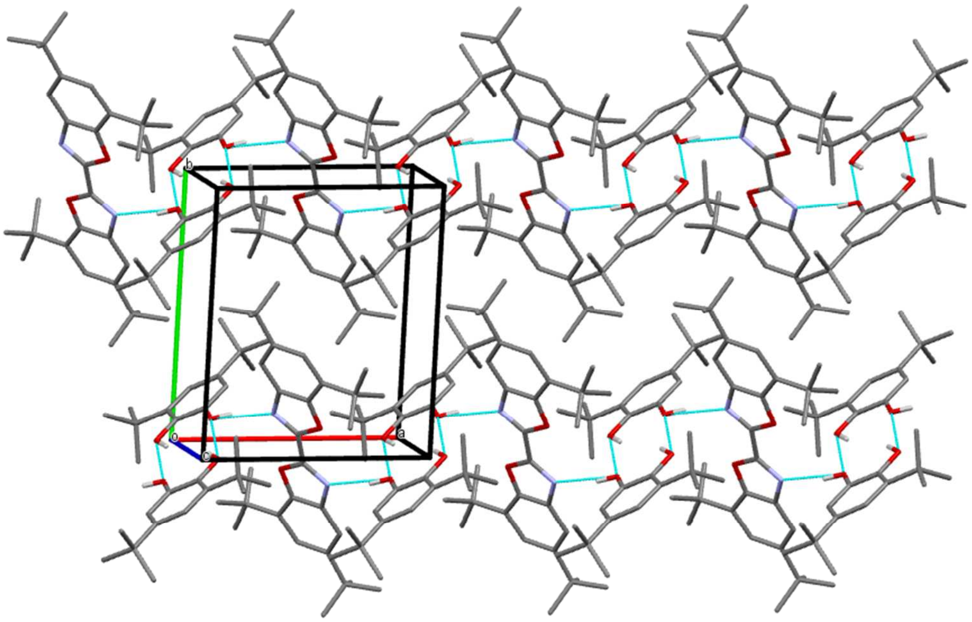


Figure 2. Crystal packing diagram of **2** showing the N…H-O and O-H…O hydrogen bonds between substituted benzoxazole and catechol. Symmetry codes: [-x, -y, -z+1], [-x+1, -y+1, -z+1]

To understand clearly how the cocrystals were generated from ethylenediamine and 3,5-di-*tert*-butylbenzoquinone, equivalent amounts of **1** and 3,5-di-*tert*-butylbenzoquinone were suspended with CH_3CN in the presence of air. Since **1** was partially soluble in CH_3CN, the mixture of **1** and 3,5-di-*tert*-butylbenzoquinone was stirred at room temperature. After 12 h of stirring, the resulting precipitate was filtered and analyzed using ^1H NMR spectroscopy. The resulting ^1H NMR spectrum is shown in Figure 3 and clearly indicated the formation of the structure in scheme 2 labeled as **3**. To further investigate the generation of **3**, various FT-IR spectra were recorded, and are shown in Figure 4. Along with bands at 3480 and 3099 cm^{-1}, which are characteristic FT-IR bands for **2**, an additional band was observed at 3367 cm^{-1}, suggesting the presence of a free amine group, and hence the structure of **3** (Scheme 2). We concluded that an insufficient amount of 3,5-di-*tert*-butylbenzoquinone led to the formation of **3** (Scheme S1). Hence two equivalents of 3,5-di-*tert*-butylbenzoquinone were added to the suspension of **1** in CH_3CN. As we expected, this amount led to the formation of **2** as a single product with excellent yield (90%) as confirmed with ^1H NMR spectroscopy (Figure 3). Moreover, in the FT-IR spectrum, the absence of –C=O stretching vibrations, shift in –OH group frequency (3480 cm^{-1}), and change in the hydrogen-bonding nature confirmed a complete conversion of 3,5-di-*tert*-butylbenzoquinone to 3,5-di-*tert*-butylcatechol when two equivalents of 3,5-di-*tert*-butylbenzoquinone were added.

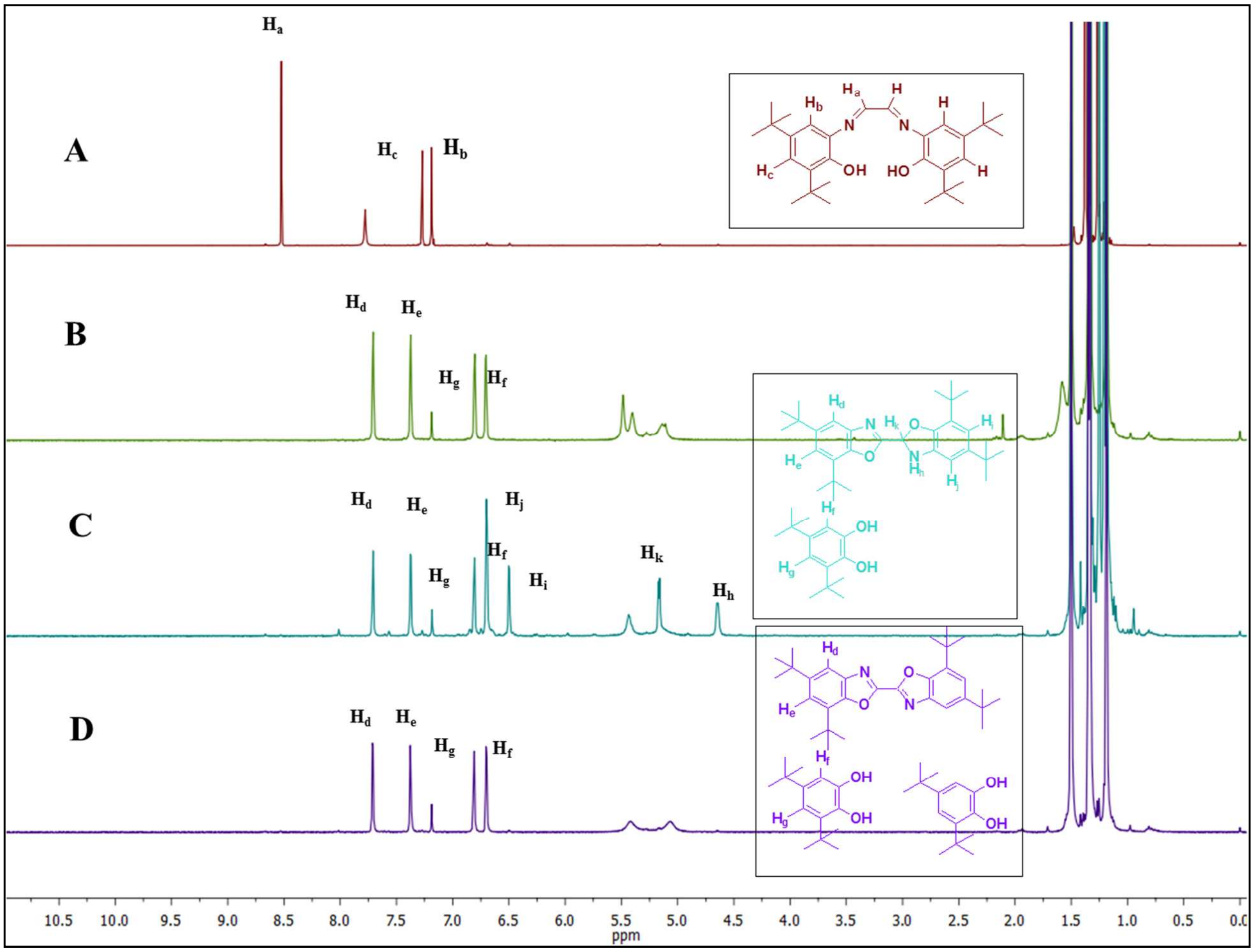


Figure 3. ^{1}H NMR spectra of A) **1**, B) **2**, C) the product of reacting **1** and 3,5-di-*tert*-butylbenzoquinone at a 1:1 ratio, and D) the product of reacting **1** and 3,5-di-*tert*-butylbenzoquinone at a 1:2 ratio

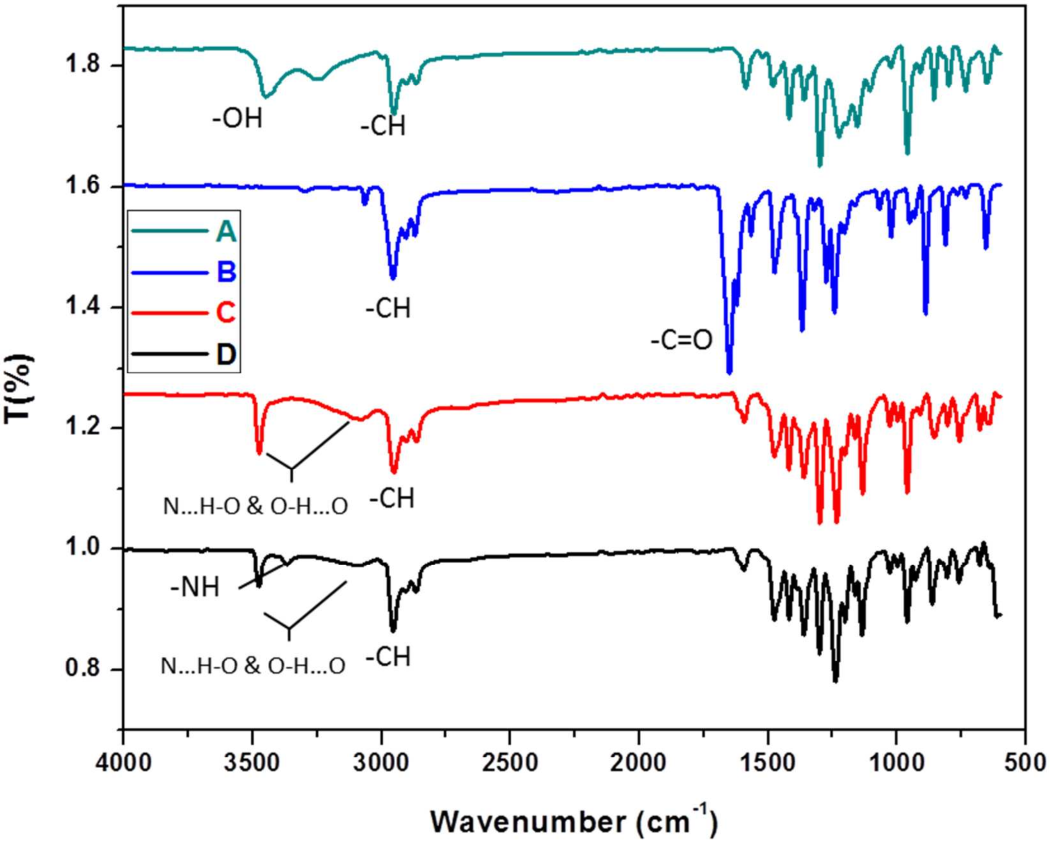
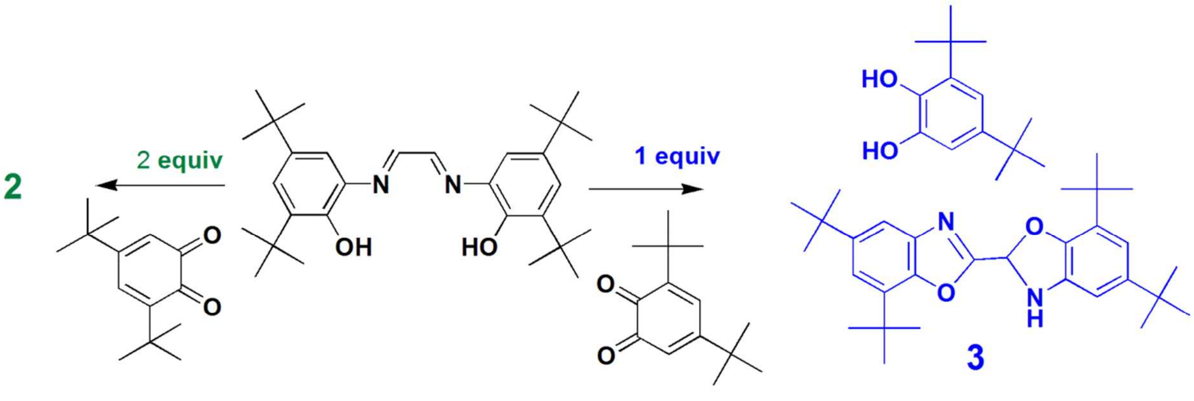
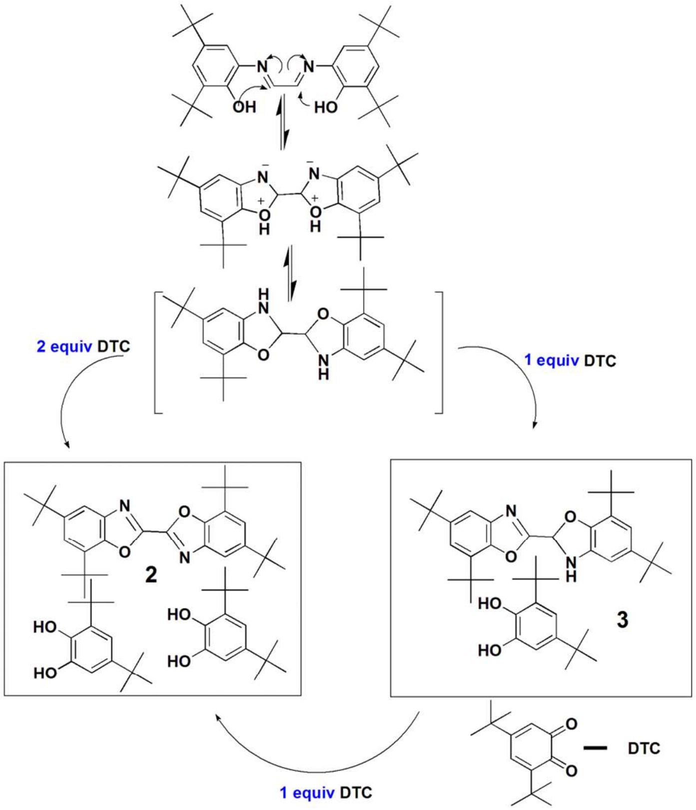


Figure 4. FT-IR spectra of A) 3,5-di-*tert*-butylcatechol, B**)** 3,5-di-*tert*-butylbenzoquinone, C) **2**, i.e., the product of reacting **1** and 3,5-di-*tert*-butylbenzoquinone at a 1:2 ratio, and D) **3**, i.e., the product of reacting **1** and 3,5-di-*tert*-butylbenzoquinone at a 1:1 ratio



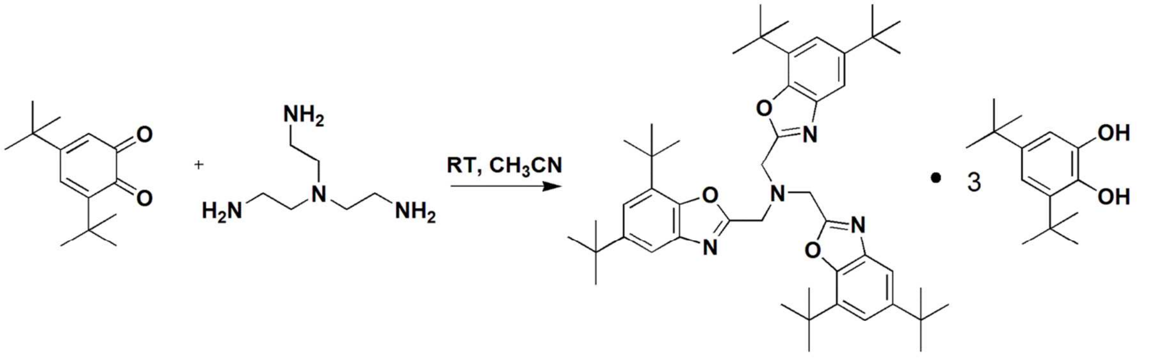
Scheme 2. Synthesis of **3**

Overall, combining two equivalents of 3,5-di-*tert*-butylbenzoquinone with one equivalent of **1** were generated cocrystals **2** as a single product. Here, the reduction of 3,5-di-*tert*-butylbenzoquinone to 3,5-di-*tert*-butylcatechol to generate cocrystals **2** required four protons and four electrons. When **1** was treated with 3,5-di-*tert*-butylbenzoquinone in an anhydrous CH_3CN medium under an inert atmosphere, **2** formed with an excellent yield, indicating that the necessary protons and electrons only came from **1** to form the stable aromatic benzoxazole ring. An investigation of the mechanism of the formation of the cocrystals using FT-IR spectroscopy and ^{1}H NMR spectroscopy suggested that the cocrystals could be obtained in excellent yield and also showed a new method to synthesize substituted benzoxazole using 3,5-di-*tert*-butylbenzoquinone as an oxidizing agent. Based on our spectroscopy studies, an inert atmosphere reaction, and the single-crystal X-ray structure, we proposed a mechanism which is shown in Scheme 3.



Scheme 3. Proposed mechanism for the generation of **2**

Using our cocrystal synthesis method, **4** was synthesized from 3,5-di-*tert*-butylbenzoquinone and tri(2-amintheyl)amine to introduce tertiary amine nitrogen in the cocrystal to enhance the CO_2 adsorption capacity (Scheme 4).



4

Scheme 4. Synthesis of **4**

Thermogravimetric analysis was employed to determine the thermal stability of **1**, **2**, **3** and 3,5-di-*tert*-butylcatechol (Figure 5). **1** degraded in two steps, with the first degradation beginning at 150 ^{o}C and ending at 175 ^{o}C with 6% of the initial weight lost. The second degradation step started at 198 ^{o}C and ended at 198 ^{o}C with cumulatively 60 % of the initial weight lost. Interestingly, **2** degraded in two steps, the first one beginning at 200 ^{o}C and the second one starting at 240 ^{o}C. To determine the effect of 3,5-di-*tert*-butylcatechol hydrogen bonding in **2**, 3,5-di-*tert*-butylcatechol was also analyzed using TGA: it started degrading at 125 ^{o}C and was fully degraded by 205 ^{o}C, i.e., without leaving any residue. These results clearly indicated that the presence of hydrogen bonds in cocrystals of substituted benzoxazole and 3,5-di-*tert*-butylcatechol increased the thermal stability of **2**. For **2** and **3**, residue amounting to about 20% of the initial weight in each case remained at 300 ^{o}C. These results provided additional evidence that hydrogen bonds between the 3,5-di-*tert*-butylcatechol and substituted benzoxazole increased the thermal stability of cocrystals **2** and **3**.

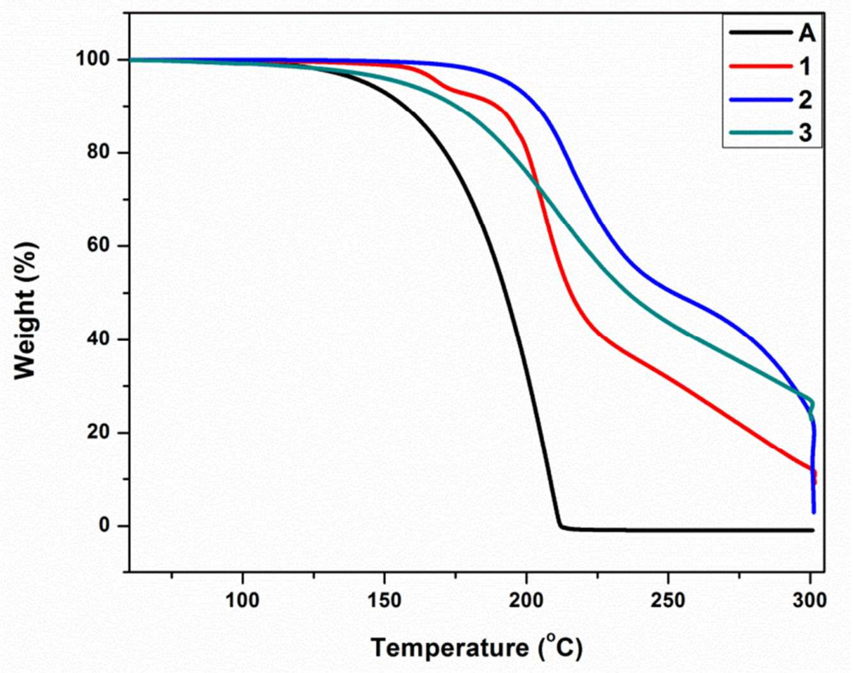


Figure 5. TGA analysis curves for 3,5-di-*tert*-butylcatechol (A)**,** and **1-3**

The synthesized cocrystals **2-4** were tested for CO_2 adsorption studies. Important properties of suitable adsorbents for CO_2 removal from flue gas are high CO_2 adsorption capacity, fast kinetics, high CO_2 selectivity, mild conditions for regeneration, stability during extensive adsorption and desorption cycling, tolerance of adsorbents to impurities in the flue gas, and low cost[37]. Initially, **2** was tested for CO_2 adsorption and desorption at room temperature and is given in Figure S5. The amount of CO_2 adsorbed by **2** was 15.96 mg/g [0.363 mmol/g] at RT (Figure 6). This result suggests that cocrystals **2** could be used as an adsorbent for CO_2 capture. The adsorption and desorption graph of **2** with CO_2 showed that **2** could be easily regenerated for subsequent cycles (Figure S5). However, the amount of CO_2 adsorbed by **2** was not high when compare to that of available adsorbents, e.g., 7.56 mmol/g for hyperbranched polyamine[26]. The CO_2 adsorption and desorption nature of **2** suggested that it could be used in the CO_2 capture process, and further modification in **2** with appropriate functional groups could increase the CO_2 adsorption capacity. Secondary amine containing **3** adsorbed CO_2 amount was 23.00 mg/g which is higher than that of **2**. The amount of CO_2 adsorbed by **4** was measured to be 44.21 mg/g, and this result clearly indicated that, as we expected, introduction of a tertiary amine into the cocrystals enhanced the CO_2 adsorption capacity. It was reported that tertiary-amine-containing adsorbent was more easily regenerate CO_2 than the primary- and secondary-amine-containing adsorbents. Although CO_2 adsorption capacity was moderate for the synthesized cocrystals **2**-**4**, we believe that further modification in the cocrystals could enhance the CO_2 adsorption capacity.

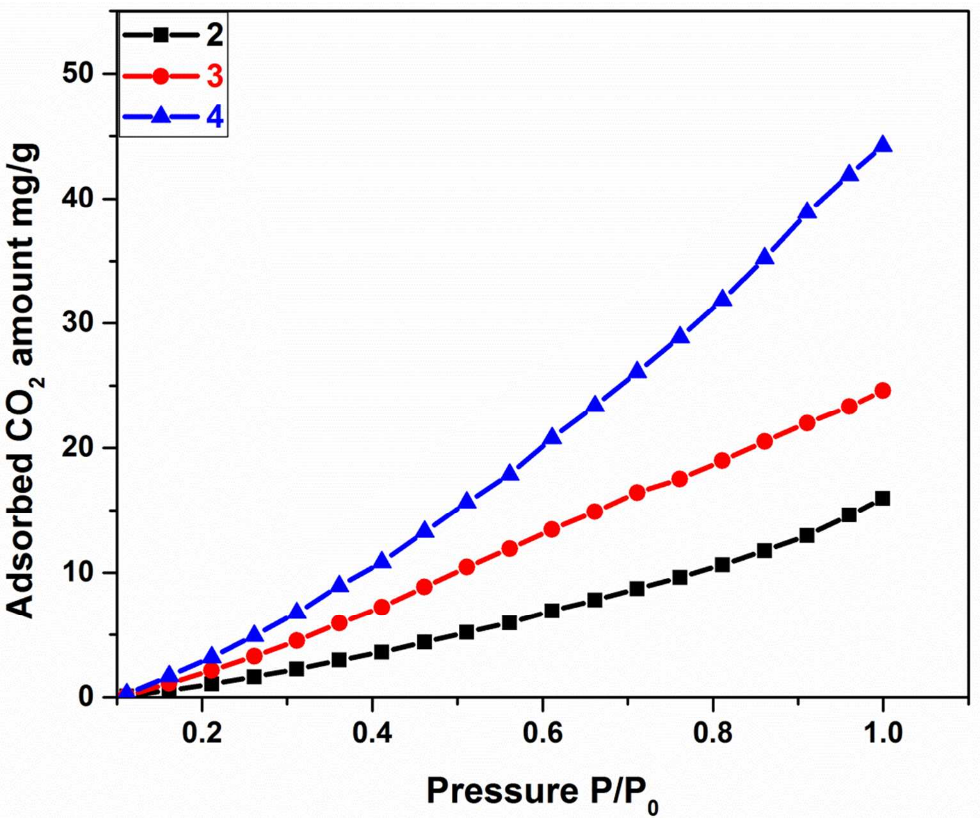


Figure 6. Adsorption of CO_2 by **2-4** in mg per adsorbent

Overall, in a single step substituted benzoxazole and catechol cocrystals were synthesized from primary amine and 3,5-di-*tert*-butylbenzoquinone, and it's a new method to synthesize substituted benzoxazole using 3,5-di-*tert*-butylbenzoquinone as an oxidizing agent. Furthermore, from **1** substituted benzoxazole and benzoxazoline could be easily synthesized by varying the equivalence of diketones. Currently, we are working on synthesis of various cocrystals from primary amines and diketones. A study of further roles of various diketones in the formation of benzoxazole is also underway.

Conclusions

In summary, we reacted a primary amine and 3,5-di-*tert*-butylbenzoquinone to form cocrystals made up of a substituted benzoxazole and a catechol. The formation of benzoxazole in **2** from **1** and benzoquinone suggested that our method should be useful in the synthesis of substituted benzoxazoles. More importantly, our CO_2 adsorption studies revealed that cocrystals **2**-**4** could be used for CO_2 capture. The higher CO_2 adsorption capacity of **4** than that of **2** suggested that the cocrystals could be easily modified to enhance the CO_2 adsorption. We expect our studies to initiate research into the syntheses of many substituted-benzoxazole- and catechol-containing cocrystals and that some of these new products will prove beneficial for CO_2 capture.

Experimental Section:

General Consideration: All chemicals purchased were of analytical grade and used without further purification. FT-IR spectra were recorded using the ATR method with a Varian 640-IR FT-IR spectrometer. ^1H NMR and ^{13}C NMR were recorded on Varian 300 MHz and Varian 125 MHz instruments, respectively.

X-ray single crystal structural analysis: A single crystal was mounted at room temperature on the tips of quartz fibers, coated with Paratone-N oil, and cooled under a stream of cold nitrogen. Intensity data were collected on a Bruker CCD area diffractometer running the SMART software package with Mo Kα radiation (λ= 0.71073). The structure was solved by direct methods and refined on F^2 using the SHELXTL software package[38]. The multi-scan absorption correction was applied with SADABS[39], which is part of the SHELXTL program package, and the structure was checked for higher symmetry by the program PLATON[40]. All non-hydrogen atoms were refined anisotropically. In general, hydrogen atoms were assigned idealized positions and given thermal parameters equivalent to 1.2 times the thermal parameter of the carbon atom to which they were attached. Data collection and experimental details for the complex **2** (CCDC 1533263) is summarized in Table S1, and bond angles and distance are summarized in Table S2.

CO_2 adsorption and desorption studies: N_2 adsorption−desorption isotherms of cocrystals were measured on a static volumetric technique instrument (gas sorption analyzer, Micromeritics ASAP 2020) for determination of the surface area, total pore volume, and the average pore diameter. Prior to measurement, approximately 100 mg of the co-crystal was degassed at 100 °C for 8 h under vacuum to eliminate humidity and trapped gases. The N_2 adsorption−desorption data were recorded at liquid nitrogen temperature, 77 K, and applied in a relative pressure (P/Po) range from 0 to 1.0. The surface areas (SBET) were calculated using the BET equation by Brunauer, Emmett, and Teller, which is the most widely used model for determining the specific surface area. All surface area measurements were calculated from the nitrogen adsorption isotherms by assuming the area of the nitrogen molecule to be 0.162 nm^2. The total pore volume (Vtot) was assessed by converting the amount of N_2 gas adsorbed (expressed in cm^3/g at STP) at relative pressure to the volume of liquid adsorbate. Multilayer CO_2 adsorbed by physisorption at

25 °C and room pressure was measured using the above-mentioned instrument with a degassing step prior to analysis. The CO_2 analysis was conducted, and a water circulating bath was used to control the temperature.

Synthesis of **1**:To a solution of 3,5-di-*tert*-butylbenzoquinone (1.46 g, 3.30 mmol) in MeCN (25 mL) was added dropwise a solution of ethylenediamine (0.200 g; 6.65 mmol) in CH_3CN (2 mL) at 0 °C in the presence of air. The resulting mixture was stirred at 0 °C for 1 h and yellow precipitate was filtered and dried under high vacuum. Yield: 0.72 g (47%). ^{1}H NMR (600 MHz, Chloroform-*d*) δ 8.52 (s, 2H), 7.72 (s, 2H), 7.27 (d, *J* = 2.2 Hz, 2H), 1.38 (s, 19H), 1.27 (s, 19H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 154.36, 150.07, 141.69, 136.00, 133.39, 125.91, 109.77, 35.03, 34.62, 31.55, 29.38. Elemental analysis; calculated for **1**; C, 77.54; H, 9.54; N, 6.03; found; C, 77.49; H, 9.45; N, 6.92. LC-Mass: calculated (M+1) = 466.00, found 466.20.

Synthesis of cocrystals[**2**]: To a solution of 3,5-di-*tert*-butylbenzoquinone (1.46 g, 3.30 mmol) in MeCN (25 mL) was added dropwise a solution of ethylenediamine (0.200 g; 6.65 mmol) in CH_3CN (2 mL) at 0 °C in the presence of air. The resulting mixture temperature was slowly brought into room temperature and stirred for 12 h. Resulting light-yellow precipitate was filtered and dried under high vacuum. Yield: 0.72 g (12%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 1.7 Hz, 2H), 7.38 (d, *J* = 1.7 Hz, 2H), 6.81 (d, *J* = 2.1 Hz, 2H), 6.71 (d, *J* = 2.1 Hz, 2H), 1.50 (s, 18H), 1.35 (s, 18H), 1.33 (s, 18H), 1.18 (s, 18H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.83, 148.93, 147.37, 142.40, 142.10, 141.57, 140.78, 135.66, 134.71, 121.77, 115.93, 115.28, 110.41, 35.22, 34.84, 34.61, 34.32, 31.75, 31.57, 30.02, 29.66, 29.32. Elemental analysis; calculated for **2;** C, 76.95; H, 9.35; N, 3.09; found; C, 76.92; H, 9.29; N, 3.11. LC-Mass: calculated (M+1) = 461.30, found 461.00.

Synthesis of **3** from **1** with 1 equivalent of 3,5-di-*tert*-butylbenzoquinone : To a mixture of imine (0.100 g, 0.215 mmol) in MeCN (2.5 mL) was added a solution of 3,5-di-*tert*-butylbenzoquinone (47.0 mg, 0.215 mmol) in CH_3CN (2 mL) at room temperature in the presence of air. The resulting mixture was stirred at RT for 12 h and yellow precipitate was filtered and dried under high vacuum. Yield: 75.82 mg. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 1.8 Hz, 1H), 7.37 (d, *J* = 1.8 Hz, 1H), 6.81 (d, *J* = 2.3 Hz, 1H), 6.70 (dd, *J* = 2.2, 1.0 Hz, 2H), 6.50 (d, *J* = 2.2 Hz, 1H), 5.43 (s, 1H), 5.16 (d, *J* = 3.7 Hz, 1H), 4.65 (d, *J* = 3.9 Hz, 1H), 1.50 (s, 9H), 1.35 (s, 9H), 1.33 (s, 9H), 1.25 (s, 9H), 1.21 (s, 9H), 1.18 (s, 9H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 148.93, 147.38, 144.59, 143.57, 142.40, 137.97, 137.59, 135.66, 134.71, 128.77, 121.77, 117.15, 115.94, 115.29, 114.71, 110.42, 110.03, 76.36, 35.23, 34.86, 34.61, 34.33, 31.76, 31.56, 30.02, 29.86, 29.86. Elemental analysis: calculated for **3**; C, 76.82; H, 9.15; N, 5.78; found; C, 75.99; H, 9.07; N, 5.68. LC-Mass: calculated (M+1) = 463.30, found 463.90.

Synthesis of **2** from **1** with 2 equivalent of 3,5-di-*tert*-butylbenzoquinone: To a mixture of imine (0.100 g, 0.215 mmol) in MeCN (2.5 mL) was added a solution of 3,5-di-*tert*-butylbenzoquinone (94.0 mg, 0.430 mmol) in CH_3CN (2 mL) at room temperature in the presence of air. The resulting mixture was stirred at RT for 12 h and yellow precipitate was filtered and dried under high vacuum. Yield: 0.174 g (90%). ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 1.7 Hz, 2H), 7.38 (d, *J* = 1.7 Hz, 2H), 6.81 (d, *J* = 2.1 Hz, 2H), 6.71 (d, *J* = 2.1 Hz, 2H), 1.50 (s, 18H), 1.35 (s, 18H), 1.33 (s, 18H), 1.18 (s, 18H). ^{13}C NMR (151 MHz, Chloroform-*d*) δ 151.83, 148.93, 147.37, 142.40, 142.10, 141.57, 140.78, 135.66, 134.71, 121.77, 115.93, 115.28, 110.41, 35.22, 34.84, 34.61, 34.32, 31.75, 31.57, 30.02, 29.66, 29.32.

Synthesis of **4**: To a solution of 3,5-di-*tert*-butylbenzoquinone (0.225 g, 1.02 mmo) in CH_3CN, tri(2-amintheyl)amine (0.050 g, 0.34 mmol) solution of CH_3CN was added at 0^{o}C and stirred for

1 h. The solution of 3,5-di-*tert*-butylbenzoquinone(0.225 g, 1.02 mmol) in CH_3CN was added in RT and stirred for 12 h. Resulting off-white crystalline solid was filtered and dried. 0.060 g, 18%. ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 1.8 Hz, 2H), 7.45 (d, *J* = 1.8 Hz, 2H), 6.88 (d, *J* = 2.2 Hz, 2H), 6.77 (d, *J* = 2.2 Hz, 2H), 2.17 (d, *J* = 0.5 Hz, 6H), 1.57 (s, 18H), 1.42 (s, 18H), 1.41 (s, 18H), 1.26 (s, 18H). ^{13}C NMR (75 MHz, Chloroform-*d*) δ 148.90, 148.66, 147.33, 146.62, 144.74, 141.61, 136.33, 134.70, 115.88, 115.30, 110.41, 78.89, 35.22, 34.84, 34.61, 34.62, 31.76, 31.57, 30.94, 30.02, 29.66. Elemental analysis: calculated for **4**: C, 76.82; H, 9.15; N, 5.78; found; C, 76.12; H, 9.05; N, 5.58. LC-Mass: calculated (M+1) = 747.51, found 747.30.

ASSOCIATED CONTENT

Supporting Information. X-ray crystallographic files of **2** in CIF format; ^{1}H and ^{13}C NMR Spectra, FT-IR spectra and Mass data and X-ray crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Substituted Benzoxazole and Catechol Cocrystals as an Adsorbent for CO_2 Capture: Synthesis and Mechanistic Studies

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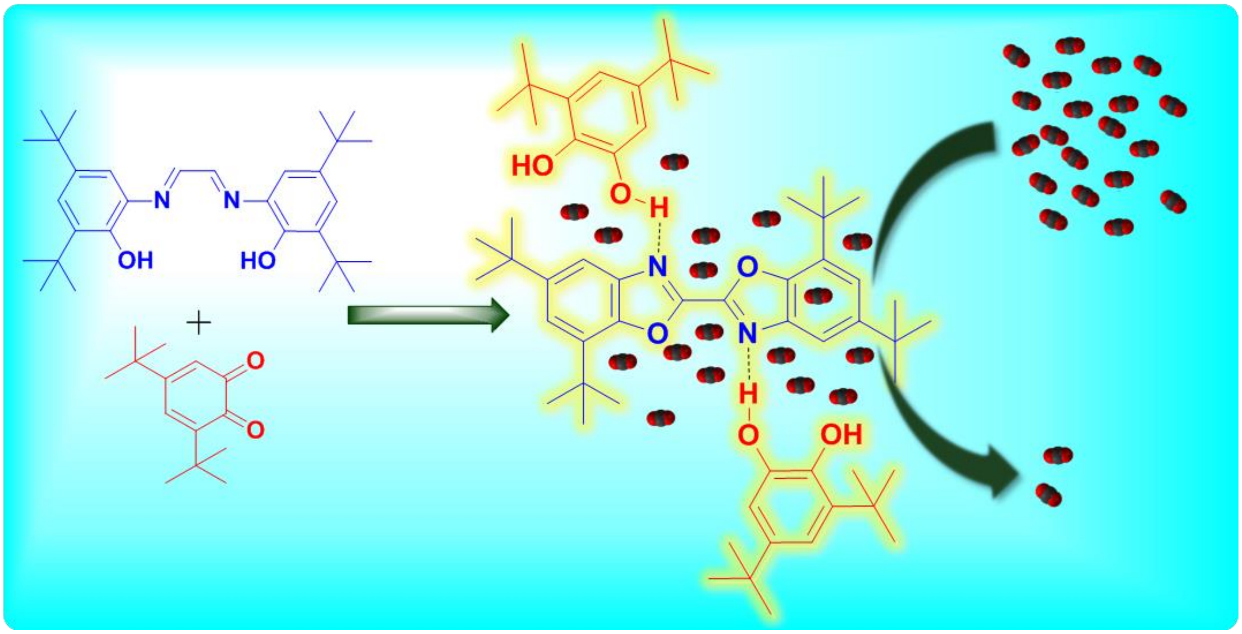
Graphical Abstract:



Synopsis:

The synthesis of cocrystals of a substituted benzoxazole and catechol from a primary amine and 3,5-di-*tert*-butylbenzoquinone is reported. By varying the equivalence of diketones, from **1** substituted benzoxazole and benzoxazoline were synthesized. Our results indicated the ability to use cocrystals for CO_2 capture and introduction of an amine into the cocrystal structure enhanced the CO_2 adsorption capacity.