

FT-IR Analysis of Pyrone and Chromene

Structures in Activated Carbon

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ABSTRACT: The behaviour of activated carbon in many catalysis processes is determined by the basic character of its surface. Using FT-IR spectroscopy, an attempt is made here to identify not only pyrone and chromene type structures but also their isomers in a commercial activated carbon (Merck; AC). The infrared analysis between 400 and 4000 cm^{-1} focuses on the keto ($-\text{C}=\text{O}$) group in pyrones, methylene ($-\text{CH}_2-$) group in chromenes, and enol ether group ($\text{O}-\text{C}=\text{C}$) in both kinds of structures. Although overlapping bands are frequent in the AC spectrum, occurrence of most significant pyrone and chromene absorptions proves their presence in AC. This is so in particular for 2-pyrone and 4H-chomene, whereas 4-pyrone is less amenable to the infrared analysis.

INTRODUCTION

Since the pioneering studies conducted by Smith¹ and by Rhead and Wheeler^{2,3} on the formation of the carbon-oxygen complex of variable composition C_xO_y , the surface chemistry of carbon has received a great deal of attention. Interest in the study of such a surface has been mainly due to its influence on catalysis,^{4,5} wetting,⁶ adsorption,⁷ electrochemical,⁸⁻¹⁰ and other properties of carbons. The various aspects of the surface

chemistry of carbon have been described before,^{8,11,12} Also, the methods used more frequently in its study were reviewed.¹³ In the C-O complex, oxygen can be bound to carbon atoms in the form of various typical organic functional groups (i.e. quinone type carbonyl, phenolic hydroxyl, carboxyl, lactone, and ether) which may be acidic or basic in character.¹⁴ The basic surface groups play an outstanding role in many carbon utilization processes. The gold cyanide uptake capacity of activated carbon noticeably increases with an increase in the content of basic surface groups.¹⁵ A basic surface chemistry made up of oxygen or nitrogen structures is required for a large number of carbon-catalyzed reactions.¹⁶ Perfect correlations have been found between the total number of basic groups and the gravimetric capacitance of carbon in electric double layer capacitor.¹⁷ However, the basic C-O surface groups of carbons in a specific manner have been very little studied. The main aspects of carbon basicity were dealt with in detail elsewhere.^{18,19} Furthermore, basic sites were thoroughly analysed by quantum chemical-based theoretical calculations with model compounds²⁰ and by elemental analysis, point of zero charge and microcalorimetric measurements.²¹ The present study focuses on the analysis of pyrone and chromene structures in commercial activated carbon (AC) by using FT-IR spectroscopy. A lactone is a cyclic ester which can be seen as the condensation product of an alcohol group and a carboxylic acid group and therefore it contains an oxygen atom and a ketone functional group. The unsaturated lactones with a six-membered ring are named pyrones. Chromene (benzopyran) is an internal ether in which a benzene ring is fused to a pyran (oxine) ring. Regarding the presence in carbons, both kinds of oxygen structures have been the object of controversy. Although the chromene structure of Garten and Weiss²² and the pyrone structure of Voll and Boehm²³ were proposed as responsible for the acid uptake, the latter authors discarded the chromene structure on the basis of experimental evidence in

favour of pyrone-like structures. Pyrones are supposed to be formed on carbon surfaces by air exposure of heat-treated carbons.¹⁸ For 800 °C-preheated carbon blacks re-exposed to air at 100 °C, it was found that the amount of chemisorbed oxygen corresponds to the amount of pyrone groups.²⁴ They are generated by thermal decomposition of oxygenated acidic groups, formation of active sites capable to fix oxygen in an ether form, and rearrangement with existing carbonyl groups which resist pyrolysis.²⁵ For carbon materials, ether type structures are thermally stable and decompose in the temperature range from ca. 500 to 800-1000 °C.²⁶ Basic functional groups may be formed as a result of the high temperature heat treatment under reductive conditions carried out in their preparation.¹⁹ Since AC is usually first prepared in one or two heat treatment stages at 350-950 °C and then kept stored under air atmosphere until use, the presence of pyrone and chromene structures in AC was viewed as foreseeable.

Although infrared spectroscopy is a valuable tool widely used in the structural analysis of chemical compounds, the spectral interpretation is frequently obscured because of overlapping bands. This is particularly true for carbonaceous materials because they usually contain various surface groups and structures which absorb energy at close frequencies, as in the spectral region of ether absorptions.²⁷ Certainly, carbon surface groups with composition and structure similarities are less amenable to the infrared analysis. For pyrone isomers and chromene isomers such as 2-pyrone structure (I), 4-pyrone structure (II), 2H-chromene structure (III), and 4H-chromene structure (IV), specifically, the chemical formula are shown in Figure 1. The 2-pyrone structure is found in nature as part of the coumarin ring system, whereas the 4-pyrone structure is present in some natural chemical compounds such as chromene, which is an isomer of coumarin (also named 1,2-benzopyrone, 2H-chromen-2-one, and so on). It is made up of a 2-pyrone ring fused to a benzene ring, as shown in Figure 2. In carbonaceous

materials, pyrone and chromene structures must be a part of graphene sheets, probably with the additional incorporation of oxygen surface groups such the carboxyl group (as an illustrative example, see Figure 2), hydroxyl group, and so on, because of a lengthy oxidation.

The spectral interpretation may also be handicapped by the fact that most spectra available in literature are calculated theoretically or obtained for commercial organic chemicals in various physical states and solvents and that thereby the number, position and intensity of absorption bands may vary significantly as compared to carbonaceous materials such as AC with a rather disordered (turbostratic) graphite structure. Despite its limitations, infrared spectroscopy was suggested as the most sensitive tool for probing hydrogen bonding in coal.²⁸

EXPERIMENTAL SECTION

A granular AC from Merck[®] (Darmstadt, Germany), 1.5 mm average particle size (Code 1.02514.1000), as received, was used. AC was characterized in terms of proximate and elemental compositions. The ash content was determined by incineration at 650 °C for about 12 h in air, using a muffle furnace (Selecta[®]). The soaking time at maximum heat treatment temperature was long enough to ensure that the material fraction contained in each sample was completely oxidized and transformed into gaseous products and residual ashes. The elemental analysis (C, H, N and S contents) was performed in an elemental analyzer (CHNS-932, LECO[®]), whereas the O content was estimated by difference. Data of the chemical analyses of AC are compiled in Table 1.

Using a Perkin Elmer[®] Spectrum 100 spectrometer, the spectrum of AC was recorded in the range of wave numbers from 4000 to 400 cm⁻¹, averaging the data of 8

successive scans taken at 2 cm^{-1} resolution. In the preparation of the pellet, AC in a series of successive steps was size-reduced for homogenization, weighed, and thoroughly mixed with KBr (Panreac[®], PAI for IR spectroscopy) at the 1:1900 sample/KBr ratio in a small size agate mortar, the pellet mass being ca. 238 mg. After that, the resulting powder mixture was placed in a Perkin Elmer[®] manual hydraulic press and compacted at $10\text{ Tm}\cdot\text{cm}^{-2}$ for 3 min. During such time period, the system was evacuated with an oil pump. The spectrum of a KBr pellet, approximately containing the same mass of KBr as the AC pellet, was used as background. The measured spectrum was baseline-corrected and smoothed according to the Savitzky-Golay method by means of a 25 point smoothing filter using the appropriate software (Perkin Elmer[®] Spectrum).

RESULTS

As seen in Table 1, the O content is by far much higher than the S and N contents for AC. Furthermore, oxygen must be predominantly found combined with carbon atoms in carbon-oxygen surface functional groups as this heteroatom usually constitutes about 90 per cent of the total amount of bound oxygen.²⁹ Accordingly, the oxygen groups should be more amenable to the IR analysis than those of nitrogen and sulphur. Nevertheless, it should be borne in mind that the N-O and N=O bonds containing nitrogen surface groups span a similar frequency range to that covered by the corresponding oxygen groups. Thus, nitrogen groups with the N-O bond can be considered to be analogs of ether type structures and the nitro group ($-\text{NO}_2$) is isoelectronic with the carboxylate ion group ($-\text{CO}_2^-$).³⁰ However, as compared to their analogous oxygen surface groups, the carbon-sulfur surface groups (i.e. C-S, C-S-H, and so on) give rise to very weak absorption bands in the infrared spectrum. Furthermore, characteristic group frequencies occur at noticeably lower frequencies for the sulfur groups as the atomic mass is higher

for sulfur than for oxygen.³¹ From these statements it becomes apparent that sulfur will not noticeably interfere with the FT-IR analysis of AC, regarding the oxygen surface groups.

The infrared spectrum obtained for AC is shown in Figures 3 and 4. It has been plotted separately for two regions in order to render the spectral features appearing between 4000 and 2000 cm^{-1} more readily visible, by using an expanded Y-axis. Between 4000 and 400 cm^{-1} it displays a number of features which are assigned as described in Table 2.

DISCUSSION

Analysis of pyrone and chromene structures. Figure 1 shows that the most important distinguishing structural molecular features between pyrones and chromenes are the keto ($-\text{C}=\text{O}$) group in pyrones and methylene ($-\text{CH}_2-$) group in chromenes. Accordingly, the infrared analysis of these groups is essential with a view to the mutual identification of pyrone and chromene structures in AC, provided that they are found in the material. In contrast, the enol ether atomic grouping ($\text{O}-\text{C}=\text{C}$) is found in both kinds of compounds. In the spectral analysis, the $\text{C}=\text{O}$ group and $-\text{CH}_2-$ group will be studied first separately for pyrones and chromenes, respectively. Then, the $\text{O}-\text{C}=\text{C}$ group will be dealt with jointly for both kinds of structures, mainly for comparison purposes.

For lactones (i.e. a cyclic ester), spatial and structural factors can be important, in particular ring stress. Conjugation plays a prominent role in the observed carbonyl frequency. This includes connection to an aromatic ring or conjugation with a $\text{C}=\text{C}$ or another $\text{C}=\text{O}$.³⁰ It is so because there is a resonance contribution leading to a greater single bond character of the carbonyl group. As a guide, the $\text{C}=\text{O}$ frequency lowers by 20 and 30 cm^{-1} depending on whether the CO group is conjugated with an aromatic

C=C or with another C=C.³² Figure 1 shows that the degree of conjugation of the C=O bond is larger for 4-pyrone than for 2-pyrone. In the case of the former isomer (i.e. for a carbonaceous material such as AC the pyrone ring must be attached to benzene rings in a graphene sheet) the C=O bond is conjugated with an aromatic C=C bond and with a pyrone-ring C=C bond, whereas for the latter isomer the C=O group is also conjugated but only with the pyrone-ring C=C bond. Moreover, it has been reported that the $\nu(\text{C}=\text{O})$ can fall dramatically because of the resonance-stabilized electron deslocalization for the 4-pyrone.³² This pyrone isomer is more basic than the 2-pyrone isomer and the stronger the basicity of the carbonyl group, usually the lower the $\nu(\text{C}=\text{O})$ band.²⁷ Differences in the molecular structure of both isomers are reflected by bond lengths and C=O stretching frequencies. The C=O bond length is 0.1184 nm for 2-pyrone and 0.1200 nm for 4-pyrone.³³ Reported vibration frequencies range between 1706 and 1740 cm^{-1} for the 2-pyrone and between 1650 and 1688 cm^{-1} for the 4-pyrone.^{27,33-40} The band was regarded as a carbonyl stretching frequency characteristic of 2-pyrone³⁵ and as specific for the carbonyl group in 4-pyrones.^{39,40} The spectrum of AC (Figure 4) displays a sharp and strong band at 1720 cm^{-1} and a greatly sloped shoulder at 1657 cm^{-1} , which are therefore compatible with the presence in the material of 2-pyrone and 4-pyrone, respectively.

Because of the vibration and bending modes of the C-H bond, the (-CH₂-) group gives rise to absorption bands at 2930 and 2850, 1470, 720, and 1350-1180 cm^{-1} region; the last being not particularly useful for molecules of any complexity.⁴¹ For the -CH₂- group bonded to an oxygen atom (-CH₂-O) in ether type structures, absorption occurs at 2835-2880 cm^{-1} .³⁴ For 2H-chromene, two spectral bands at 2970 and 2840 cm^{-1} were reported elsewhere.⁴² As far as 4H-chromene is concerned, two weak bands were also registered at 3010 and 2800 cm^{-1} .⁴³ Therefore, the three peaks at 2972, 2883 and

2823 cm^{-1} in the spectrum of AC (Figure 3) are ascribable to the $\nu(\text{C-H})$ vibration in the $-\text{CH}_2-$ group. Notice that the peak at 2972 cm^{-1} is nearly at the same frequency as the band at 2970 cm^{-1} for 2H-chromene. It also applies to the shoulder at 3014 cm^{-1} with respect to the band at 3010 cm^{-1} for 4H-chromene. Accordingly, these FT-IR results prove the presence of both chromene isomers in AC. It is supported by the weak peak at 1442 cm^{-1} in the aforementioned spectrum, which is attributable to the $\delta(\text{C-H})$ in the $-\text{CH}_2-\text{C}=\text{C}$ atomic grouping.³⁴ Band assignments to carbon-hydrogen surface groups other than the $-\text{CH}_2-$ group seem to be less likely. Although the methyl group ($-\text{CH}_3$) also absorbs in the same spectral region as the $-\text{CH}_2-$ group (i.e. 2925 and 2870 cm^{-1}),⁴¹ the $-\text{CH}_3$ group must be thermally unstable under the heating conditions used in the preparation of AC and therefore it should not be found as a surface group in this carbon. However, the spectral appearance of bands around 2900 cm^{-1} due to OH groups involved in hydrogen bonding seems to be more probable.

If pyrone and chromene structures are found in AC, the enol ether atomic grouping ($\text{O}-\text{C}=\text{C}$) should absorb because of the C-H group, olefinic C=C bond, and ether C-O-C bond. Regarding the $=\text{C}-\text{H}$ group, the $\nu(\text{C-H})$ vibration should result in a weak band between 3080 and 3020 cm^{-1} .³² In fact, bands at 3076-3128 cm^{-1} and at 3040 cm^{-1} were previously reported for 5,6-benzo-2-pyrone³⁷ and 2H-chromene.⁴² respectively. In the spectrum of AC (Figure 3) only a very broad band is registered between approximately 3500 and 3000 cm^{-1} . However, the band displays various readily visible shoulders slightly above 3000 cm^{-1} , the one at 3025 cm^{-1} may be due to the $\nu(\text{C-H})$ vibration in the enol ether group.⁴¹ Absorption in the same spectral region may be also associated with the $\nu(\text{C-H})$ vibration in aromatic rings of graphene sheets, as seen below.

The $\nu(\text{C}=\text{C})$ vibration mode occurs in the spectral region of 1430 to 2000 cm^{-1} . For the C=C bond, as for the C=O bond, conjugation also originates a fall in the stretching frequency. It is slight and of approximately 40 to 60 cm^{-1} depending on whether the C=C bond is conjugated with an aromatic nucleus and with another C=C or C=O, respectively.⁴¹ From Figure 1 it follows that the C=C bond is conjugated with an aromatic C=C bond for 2-pyrone and 2H-chromene and with the C=O bond for 4-pyrone, whereas for 4H-chromene there is not conjugation of the C=C bond. Accordingly, the expected shift of the C=C band as a result of conjugation should vary by the order: 2-pyrone \approx 2H-chromene > 4-pyrone > 4H-chromene. Reported vibration frequencies for the C=C bond are 1650~1620 cm^{-1} for 2-pyrone,²⁷ 1650~1600 cm^{-1} for 4-pyrone,²⁷ 1644 cm^{-1} for 2H-chromene,⁴² and 1655 cm^{-1} for 4H-chromene.⁴² Accordingly, except for 2-pyrone and 4-pyrone, there is agreement between conjugation and band positions. On the other hand, obtained C=C bond lengths are 132.7 and 133.5 pm for the C₅=C₆ bond and C₃=C₄ bond, respectively, in the case of 2-pyrone and 132.7 pm for 4-pyrone. Observed band positions are 1624 and 1543 cm^{-1} for 2-pyrone and 1639 cm^{-1} for 4-pyrone.³³ Notice that the band at 1543 cm^{-1} in the spectrum of 2-pyrone is the corresponding one to the C=C bond with a bond length of 133.5 pm. From these results it becomes apparent that 2-pyrone must absorb at lower frequencies than 4-pyrone because of conjugation and bond lengths. In the spectrum of AC (Figure 4, Table 2), a shoulder is registered at 1636 cm^{-1} which is compatible with absorption by the various pyrone and chromene isomers. In addition, 2-pyrone may also contribute to the absorption below 1600 cm^{-1} .

Although the C=C absorption has been used in the characterization of the 2-pyrone structure³⁵ and as diagnostic peak for 2H-chromene⁴² in connection with the spectral assignment to pyrones and chromenes it should be borne in mind that the

$\nu(\text{C}=\text{C})$ vibration may be influenced by factors other than conjugation. The position and intensity of the $\text{C}=\text{C}$ band are very sensitive to solvent, substitution, and so on, effects. Reversed positions of the $\text{C}=\text{O}$ and $\text{C}=\text{C}$ bands have been previously reported.^{38,44} By the use of solvent shifts, Bellamy and Rogasch showed that for 4-pyridones absorption occurs at 1590 cm^{-1} for the $\text{C}=\text{O}$ bond and at 1650 cm^{-1} for the $\text{C}=\text{C}$ bond, as the $\text{C}=\text{C}$ bond is less polar than the $\text{C}=\text{O}$ bond.⁴⁵ Furthermore, a band registered at 1678 cm^{-1} for free 2,6-dimethyl-4-pyrone in solution was identified with the $\text{C}=\text{C}$ bond and a band at 1639 cm^{-1} with the $\text{C}=\text{O}$ bond. The $\text{C}=\text{C}$ band at 1678 cm^{-1} shifted to 1645 cm^{-1} upon complexation.⁴⁴ Concerning chromenes, it was stated that the position of the peak at 1644 cm^{-1} for 2H-chromene is greatly affected by substituent, especially on C-4. It moves to higher frequencies by electron donating groups, in particular for strong activating groups such as the $-\text{OH}$ group; whereas the opposite holds for electron withdrawing groups.⁴¹ Of course, the fusion of the pyrone and pyran rings to aromatic rings in graphene sheets of carbon materials must also affect bond vibration frequencies. Thus, the determined $\text{C}=\text{C}$ frequency for gas-phase 4H-pyran was 1694 cm^{-1} .⁴⁶

Identification of ether groups from infrared is not easy because organic compounds frequently contain other $\text{C}-\text{O}$ bonds, e.g. alcohols, acids, and so. Ethers usually absorb at $1275\sim 1200\text{ cm}^{-1}$ and at $1150\sim 1070\text{ cm}^{-1}$ because of the $\nu_{\text{as}}(\text{C}-\text{O}-\text{C})$ and $\nu_{\text{s}}(\text{C}-\text{O}-\text{C})$ vibrations. Of these vibrations, the latter is weaker than the former.²⁷ Regarding the $\nu_{\text{as}}(\text{C}-\text{O}-\text{C})$ vibration, bands at 1273 for 4H-chromene^{42,43} in the range $1220\text{--}1262\text{ cm}^{-1}$ for 2H-chromene⁴² and at 1200 cm^{-1} ³⁵ and 1231 cm^{-1} ³⁷ for 2-pyrone have been reported before. The peak at 1230 cm^{-1} , as the $\nu(\text{C}=\text{C})$ peak at 1644 cm^{-1} , was regarded as one the most valuable diagnostic spectral feature for 2H-chromene.³⁷ For 2-pyrone, bands at 1242 and 1122 cm^{-1} were attributed to the vibration of the C_6-O and C_2-O bonds with a bond length of 133.9 and 136.3 pm , respectively.³³ For 4-pyrone, the

length of the C-O bond is 134.2 pm and no absorption band due to this bond stretch is registered between 1300 and 950 cm^{-1} because of molecular symmetry.⁴⁷ Accordingly, only a symmetry loss by substitution in the pyrone ring would give rise to spectral bands in the aforesaid spectral range. In the case of 4-pyrone, the observed band for the $\nu(\text{C-O-C})$ vibration was at 923 cm^{-1} .³³ In brief, the $\nu_{\text{as}}(\text{=C-O-C})$ frequency follows the sequence 4H-chromene > 2H-chomene > 2-pyrone >> 4-pyrone.^{33,35,37,42,43} Figure 4 shows that the spectrum of AC displays a strong band at 1279 cm^{-1} and two (one of them badly visible) shoulders around 1249 cm^{-1} . These spectral features are compatible with the presence in the material of 4H-chromene, 2H-chromene, and 2-pyrone. The position and intensity of the 1279 cm^{-1} band strongly suggest that 4H-chromene contributes to the absorption in this spectral region, which is further supported by previously reported results.^{42,43} For 4-pyrone, it is seen in the spectrum that the band at 901 cm^{-1} becomes broader towards increasing frequencies and therefore overlapping bands involving the band at 923 cm^{-1} of 2-pyrone is possible. In the spectral region of the $\nu(\text{C-O-C})$ vibration, a band at 1050 cm^{-1} ⁴² and a series of three unassigned strong bands at 1180, 1115 and 1050 cm^{-1} ⁴³ were reported for 4H-chromene. Likewise, bands at 1126 cm^{-1} ³³ and at 1140-1179 and 1124-1159 cm^{-1} ³⁵ were shown in 2-pyrones spectra. Therefore, the four medium intensity bands shown by the spectrum of AC between 950 and 1200 cm^{-1} also support the presence of chromene and pyrone structures in the material.

Spectral features registered between 400-1000 cm^{-1} , which have been assigned as shown in Table 2, are also attributable to pyrone and chromene type structures. One such feature is the broad and strong band centred at 1024 cm^{-1} as the C-H bond of the pyrone ring absorbs near 1000 cm^{-1} because of the $\gamma(\text{C-H})$. Another is the strong peak at 740 cm^{-1} as a relatively strong band at 738 cm^{-1} was ascribed to the $\delta(\text{C-H})$ in the

pyrone ring of 5,6-benzo-2-pyrone.³⁷ Likewise, a strong band at 755 cm⁻¹ and another weak band at 740 cm⁻¹ were reported for 4H-chromene.⁴³ Similarly to the spectrum of AC, the spectrum of the aforementioned pyrone also exhibited two bands at 668 and 612 cm⁻¹, which were attributed to deformations of the pyrone ring.³⁷

Other band assignments. Besides the above-assigned peaks at 2972, 2883 and 2823 cm⁻¹, the Y-axis expanded spectrum of AC (Figure 3) displays a broad band between 4000 and 3467 cm⁻¹ with peaks at 3714, 3671 and 3637 cm⁻¹, a weak band at 3452 cm⁻¹, and a number of shoulders at lower frequencies between 3435 and ~3000 cm⁻¹, which are attributable to the $\nu(\text{O-H})$ vibration in OH groups. Most spectral features between 3435 and ~3000 cm⁻¹ are ascribable to the $\nu(\text{O-H})$ vibration in OH groups associated by hydrogen bonding. Since air-exposed carbonaceous materials usually contain surface hydroxyl groups and carboxyl groups, it can be presumed that these groups participate in the formation of hydrogen bonds. The carboxyl group can behave dually as an acidic group and as a basic group and as a result it absorbs at 3520 cm⁻¹ for the monomer and in a wide frequency range between 3400 and 2500 cm⁻¹ for the dimer.³² According to their strength, four general types of hydrogen-bonded structures were proposed by Painter et al.²⁸ involving hydroxyl groups in coal. Regarding AC, the spectral appearance of various shoulders between 3435 and ~3000 cm⁻¹ indicates that hydrogen bonds of varying bonding distance are formed. For O-H...O bonds the maximum allowable O...O distance is ~3 Å³² and that of the hydrogen atom from the O...O vector is only about 0.3 Å.⁴⁷ Likewise, it advocates for the formation of hydrogen bonding with involvement of not only the O-C (ether) bond but also of the C=O (ketone) bond. As reported elsewhere, the intramolecular hydrogen bond OH...O=C is weak and has ionic nature in 3-hydroxy-2-methyl-4-pyrone (maltol).⁴⁸ For alkanol hydroxyl groups a hydrogen bond in its optimum geometry is only slightly

stronger when formed to a ketone group than to an ether group.⁴⁹ Moreover, in the formation of hydrogen bonding lactones almost unchangeably bond to the carbonyl group rather than to the C-O-C group, presumably because of their relative proton donor powers.⁴⁷ In fact, the C-O-C bond is an electron-attracting group with negative inductive effect (-I) and positive mesomeric effect (+M). Due to the latter effect, the basic strength of the ketone group (i.e. resonance weakens the carbonyl group) should increase in pyrone structures and the acidic strength of the OH group should decrease in pyrone and chromene structures. For 4H-chromene not only the ethereal O atom but also the C-2, C-3 π bond is electron-donating, and therefore hydrogen bonding must be particularly weak for this chromene isomer. Accordingly, it may be presumed that hydrogen bonding is stronger for pyrones than for chromenes and consistently the former structures should absorb at lower frequencies, which is relevant to point out in connection to the assignment of the 3435 \sim 3000 cm^{-1} shoulders. On the other hand, for unusually strong hydrogen bonds the $\nu(\text{OH})$ band is easily missed in the spectra as it is both very weak and very broad.³² On the other hand, hydrogen bonding may be formed not only with the involvement of the C-OH group but also of the N-OH group. The oximes of benzoquinone and 1,4-naphthaquinone in the solid state show strong and broad bands centred around 2900 cm^{-1} , bearing several peaks, which were assigned to the stretching of hydrogen-bonded OH groups.⁵⁰ As a final comment, it should be pointed out that the shoulder at 3055 cm^{-1} may be originated by the $\nu(\text{C-H})$ vibration in graphene sheets of AC.

The strong band exhibited by the spectrum of AC at 1720 cm^{-1} (Figure 4) is attributable to the $\nu_{\text{as}}(\text{C=O})$ vibration not only in 2-pyrone type structures, as described above, but also in carboxylic acid functional groups.^{30,51,52} In fact, the 1710-1760 cm^{-1} band was associated with $\nu(\text{C=O})$ vibrations of lactonic and carboxylic groups.⁵³ For the

carboxylic acid groups, evidence of the band assignment was provided earlier by an ion exchange process with NaOH solution as the aforesaid band shifted to approx. 1570 cm^{-1} owing to the formation of the corresponding carboxylate anion ($-\text{COO}^-$) salt.⁵¹ The C=O band is usually centred at 1760 cm^{-1} (monomer) and at 1710 cm^{-1} (dimer).²⁷ The formation of a strong hydrogen bonding in the dimer should weaken the C=O bond (and also the O-H bond, as seen above) and this leads to broad peaks at lower frequencies. Besides the band at 1710 cm^{-1} , dimerization results in two bands at 1420 and $1300\sim 1200\text{ cm}^{-1}$ because of the coupling between the $\delta(\text{O-H})$ and $\nu(\text{C-O})$ and in a broad, medium intensity band at 920 cm^{-1} due to the $\gamma(\text{O-H})$. The latter band was regarded as a fairly evidence of the presence of the COOH dimer.²⁸ Accordingly, compatible with the presence of the carboxyl group in AC are also the strong band at 1279 cm^{-1} and the medium intensity band at 901 cm^{-1} registered in its spectrum. Although dimerization with involvement of two $-\text{COOH}$ groups bonded to two adjacent carbon atoms belonging to rings other than the pyrone ring should not be ruled out, it would be less feasible in solid state than in liquid and gas phases between individual molecules. However, hydrogen bonding may also be formed with involvement of the 2-pyrone structure, i.e. between a $-\text{COOH}$ group in C-3 and an OH group in C-4 and the C=O (ketone) group in C-2 (both O-H and C=O groups of the carboxyl group would take part at the same time in such a bond). From these statements it becomes clear that the presence of COOH groups in AC does not exclude at all that of 2-pyrone structures but, on the contrary, both oxygen surface groups would mutually stabilize. Moreover, it would account for the fact that carboxylic acid groups are frequently observed in carbonaceous materials, as studied by FT-IR spectroscopy. On the other hand, The sloped shoulder at 1657 cm^{-1} (Figure 4) may be associated with the C=O group in configurations other than 4-pyrone, such as aryl ketones or quinones which absorb at

1650-1700 cm^{-1} ⁵⁴ and at 1675 cm^{-1} ,^{27,41} respectively. For the quinone oxime structure, specifically, the band due to the $\nu(\text{C}=\text{O})$ vibration was between 1668 and 1618 cm^{-1} in solid state.⁵⁰

Between 1616 and approx. 1300 cm^{-1} the spectrum of AC exhibits a band at 1566 cm^{-1} , two weak peaks at 1470 and 1442 cm^{-1} , and two badly visible shoulders at 1386 and 1368 cm^{-1} . For carbonaceous materials, the spectrum usually displays a band slightly below 1600 cm^{-1} , which has not been yet univocally assigned. As pointed out by Moreno-Castilla et al.,⁵⁵ the band at 1580 cm^{-1} does not admit an unequivocal interpretation, being assigned to C=C stretching highly conjugated to carbonyl groups. As the two most probable assignments, the band at 1600 cm^{-1} was attributed to aromatic ring stretching or to highly conjugated, hydrogen-bonded carbonyl.⁵⁶ A peak at 1580 cm^{-1} was also assigned to aromatic C=C stretching vibrations augmented by adsorbed oxygen, either by inducing sufficient asymmetry into the polyaromatic network to allow IR inactive C=C modes to become active, or by increasing the extinction coefficient due to an increase in the dipole moment associated with these ring vibrations.^{52,57} On the basis of theoretical results obtained by Fuente et al.²⁰ the band at 1600 cm^{-1} was assigned to C=C stretching of carbon ring decorated mainly with phenolic groups in the case of acidic carbons and with cyclic ethers for basic carbons. Pyrone-like structures of different topology were proposed as simple functional groups. In the spectrum of AC (Figure. 4) the aforementioned band is centred at 1566 cm^{-1} . It is peaked at a significantly lower frequency as compared to 1580 cm^{-1} and deals with a broad (i.e. markedly broader than the bands usually registered for the individual molecules of organic substances, such as benzene or benzoic acid) and strong band, which denotes contribution of bond vibrations other than the aromatic C=C stretch to the absorption at close frequencies. Accordingly, the band is ascribable to $\nu(\text{C}=\text{C})$ vibrations in benzene

rings and 2-pyrone rings, as described above. Absorption at 1520-1570 cm^{-1} to some extent may be also associated with the C=N group, as strong bands in this spectral region were found in the spectra of a quinone oxime and of two oxime ethers. The absorption at small wave numbers was explained in terms of a strong conjugation with the quinonoid double bonds, particularly the C=O group, and subsequent reduction of the double-bond character of the C=N bond. A band at 1440 cm^{-1} was also taken as the position of the $\delta(\text{O-H})$ in quinone oxime spectra.⁵⁰ The shoulders at 1386 and 1368 cm^{-1} are attributable to the $\delta(\text{O-H})$ in phenolic and carboxylic acid groups. Usually, this band shifts to higher frequencies with strong hydrogen bonds.²⁷

At lower frequencies between 1300~1200 cm^{-1} , besides chromene and pyrone structures, the $-\text{COOH}$ group also absorbs because of the $\delta(\text{O-H})$ and $\nu(\text{O-H})$. This statement mainly concerns the strong band at 1279 cm^{-1} in the spectrum of AC (Figure 4) which has been associated as well with 4H-chromene. Likewise, the shoulder at 1209 cm^{-1} in such a spectrum can originate from the phenolic hydroxyl group which usually absorbs at 1200 cm^{-1} because of the $\nu(\text{C-O})$ vibration.²⁷ However, the medium intensity-strong bands at 1166, 1114, 1069, and 1024 cm^{-1} deserve different assignments. Bands at nearby frequencies were ascribed to $\nu(\text{C-O})$ in aromatic ethers,²⁷ $\delta(\text{C-H})$ in 2-pyrone,³⁷ $\nu(\text{N-O})$ in quinone oximes,⁵⁰ and so on. Unassigned bands were associated with phenols and quinone.⁵⁸ For 2-pyrone, the $\delta(\text{C-H})$ may occur in the phenyl ring or the pyrone ring.³⁷ In connection with band assignments it should be also taken into account the possible formation of oxygen surface groups as a consequence of a very slow but lengthy oxidation of AC by air. Different intermediate groups may be formed prior to becoming $-\text{COOH}$ groups. As a guide, it is worth noting that a variety of oxidizing substances are (i.e. H_2O_2 , O_3 , etc.) are able to attack the double bond of

chromenes to give products of differing degrees of oxidation.⁵⁹ Finally, in the spectral region around 1069 and 1024 cm^{-1} may also absorb components of the inorganic fraction of AC because of vibrations of Al-O and Si-O bonds.⁶⁰

A number of the wide series of spectral features registered in the spectrum of AC (Figure 4) between approx. 900 and 700 cm^{-1} must arise from the $\gamma(\text{C-H})$ in substituted benzene rings, as described in Table 2.^{27,61} The spectra of quinone oximes display several strong bands in the region between 700 and 900 cm^{-1} due to the $\gamma(\text{C-H})$. Furthermore, the $\gamma(\text{O-H})$ band was identified with a band at 825 cm^{-1} in the case of 1,4-naphthaquinone oxime.⁵⁰ The shoulder at 625 cm^{-1} is compatible with OH groups associated by hydrogen bonding.²⁷ Also, the peak at 530 cm^{-1} may due to the $\delta(\text{C=O})$. As an alternative assignment, it may be originated by inorganic matter of AC.⁶⁰

CONCLUSIONS

The presence of pyrone and chromene type structures in AC is proved by the fact that their significant absorption features as a rule are observed in the spectrum registered for this carbon material. Of both couples of isomers, 2-pyrone and 4-chromene are more amenable to identification by FT-IR spectroscopy, whereas the most elusive one is 4-pyrone. The infrared analysis has also enabled to identify other surface groups and structures not only of oxygen but also of nitrogen. FT-IR spectroscopy has demonstrated to be a valuable tool for the analysis of surface groups of carbon, even when they have a very similar composition and molecular structure. Overlapping bands occurs in almost all spectral regions, being more important in that of ether absorptions. In the spectral region of approx. 1600-1650 cm^{-1} , the studied isomers of pyrone and chromene absorb at close frequencies.

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Notes

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REFERENCES

- (1) Smith, A. *Proc. Roy. Soc. (London)* **1862-1863**, 12, 424-426.
- (2) Rhead, T. F. E.; Wheeler, R. V. *J. Chem. Soc. Trans.* **1912**, 101, 846-856.
- (3) Rhead, T. F. E.; Wheeler, R. V. *J. Chem. Soc. Trans.* **1913**, 103, 461-489.
- (4) Radovic, L. R.; Rodríguez-Reinoso, F. In *Chemistry and Physics of Carbon*; Thrower, P. A., Ed.; Marcel Dekker: New York, 1997; Vol. 25, pp 243-258.
- (5) Serp, P.; Figueiredo, J. L. *Carbon Materials for Catalysis*; John Wiley & Sons: Hoboken, NJ, 2009.
- (6) Steele, W. A. In *Adsorption by Carbons*; Bottani, E. J.; Tascón, J. M. D., Eds.; Elsevier: Amsterdam, 2008; pp 167-185.
- (7) Radovic, L. R.; Moreno-Castilla, C.; Rivera-Utrilla, J. In *Chemistry and Physics of Carbon*; Radovic, L. R., Ed.; Marcel Dekker: New York, 2001; Vol. 27, pp 227-405.
- (8) Leon y Leon, C. A.; Radovic, L. R. In *Chemistry and Physics of Carbon*; Thrower, P. A., Ed.; Marcel Dekker: New York, 1994; Vol. 24, pp 213-310.

- (9) Biniak, S.; Swiatkowski, A., Pakula, M. In *Chemistry and Physics of Carbon*; Radovic, L. R., Ed.; Marcel Dekker: New York, 2001; Vol. 27, pp 125-225.
- (10) Bolzán, A. E.; Arvia, A. J. In *Adsorption by Carbons*; Bottani, E. J.; Tascón, J. M. D., Eds.; Elsevier: Amsterdam, 2008; pp 479-512.
- (11) Bansal, R. C.; Donnet, J. B.; Stoeckli, F. *Active Carbon*; Marcel Dekker: New York, 1988.
- (12) Bansal, R. C.; Donnet, J. B. In *Carbon Black*; Bansal, R. C.; Donnet, J. B.; Wang, M. J., Eds.; Marcel Dekker: New York, 1993; pp 175-220.
- (13) Boehm, H. P. *Carbon* **2002**, *40*, 145-149.
- (14) Cookson, J. T. Jr. In *Carbon Adsorption Handbook*; Cheremisinoff, P.N.; Ellerbusch, F., Eds.; Ann Arbor Sci.: Ann Arbor, MI, 1980; pp 241-279.
- (15) Papirer, E.; Polania-Leon, A.; Donnet, J. B.; Montagnon, P. *Carbon* **1995**, *33*, 1331-1337.
- (16) Figueiredo, J. L.; Pereira, M. F. R. *Catal. Today* **2010**, *150*, 2-7.
- (17) Seredych, M.; Hulicova-Jurcakova, D.; Lu, G. Q.; Bandosz, T. J. *Carbon* **2008**, *46*, 1475-1488.
- (18) Montes-Morán, M. A.; Suárez, D.; Menéndez, J. A.; Fuente, E. *Carbon* **2004**, *42*, 1219-1225.
- (19) Montes-Morán, M. A.; Suárez, D.; Menéndez, J. A.; Fuente, E. In *Novel Carbon Adsorbents*; Tascón, J. M. D., Ed.; Elsevier: Amsterdam, 2012, pp 173-203.

- (20) Fuente, E.; Menéndez, J. A.; Díez, M. A.; Suárez, D.; Montes-Morán, M. A. *J. Phys. Chem. B* **2003**, *107*, 6350-6359.
- (21) Menéndez, J. A.; Phyllips, J.; Xia, B.; Radovic, L. R. *Langmuir* **1996**, *12*, 4404-4410.
- (22) Garten, V. A.; Weiss, D. E. *Rev. Pure Appl. Chem.* **1967**, *7*, 69-122.
- (23) Boehm, H. P.; Voll, M. *Carbon* **1970**, *8*, 227-240.
- (24) Papirer, E.; Dentzer, J.; Li, S.; Donnet, J. B. *Carbon* **1991**, *29*, 69-72.
- (25) Papirer, E.; Li, S.; Donnet, J. B. *Carbon* **1987**, *25*, 243-247.
- (26) Jankowska, H.; Swiatkowski, A.; Choma, J. *Active Carbon*; Ellis Horwood: Chichester, UK, 1991.
- (27) Nakanishi, N. *Infrared Absorption Spectroscopy-Practical-*; Holden-Day: San Francisco, 1962.
- (28) Painter, P. C.; Sobkowiak, M.; Youtcheff, J. *Fuel* **1987**, *66*, 973-978.
- (29) Van der Plas, Th. In *Physical and Chemical Aspects of Adsorbents and Catalysts*; Linsen, B. G., Ed.; Academic Press: London, 1970; pp 425-469.
- (30) Coates, J. In *Encyclopedia of Analytical Chemistry*; Meyers, R. A., Ed.; John Wiley & Sons: Chichester, UK, 2000; pp 10815-10837.
- (31) Gutsche, C. D.; Pasto, D. J. *Fundamentos de Química Orgánica*; Reverté: Barcelona, 1979.
- (32) Brand, J. C. D.; Eglinton, G. *Applications of Spectroscopy to Organic Chemistry*; Oldbourne Press: London, 1965.

- (33) Seixas de Melo, J.; Quinteiro, G.; Pina, J.; Breda, S.; Fausto, R. *J. Mol. Struct.* **2001**, 565-566, 59-67.
- (34) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tablas para la Elucidación Estructural de Compuestos Orgánicos por Métodos Espectroscópicos*; Alhambra: Madrid, 1980.
- (35) Wiley, R. H.; Esterle, J. G. *J. Org. Chem.* **1957**, 22, 1257-1259.
- (36) El-Kholy, I. S.; Rafla, F. K.; Soliman, G. *J. Chem. Soc. (Resumed)* **1961**, 4490-4498.
- (37) Mary, Y. S.; Panicker, C. Y.; Varghese, H. T. *Orient J. Chem.* **2012**, 28, 1071-1075.
- (38) Cook, D. *Can. J. Chem.* **1963**, 41, 522-526.
- (39) Light, R. J.; Hauser, C. R. *J. Org. Chem.* **1960**, 25, 538-546.
- (40) El-Kholy, I. S.; Rafla, F. K.; Soliman, G. *J. Chem. Soc. (Resumed)* **1962**, 1857-1863.
- (41) Pasto, D. J.; Johnson, C. R. *Organic Structure Determination*; Prentice-Hall: Englewood Cliffs, NJ, 1969.
- (42) Schweizer, E. E.; Meeder-Nycz, D. In *Chemistry of Heterocyclic Compounds*; Ellis, G. P., Ed.; John Wiley & Sons: New York, 1977; pp 11-139.
- (43) Parham, W. E.; Huestis, L. D. *J. Am. Chem. Soc.* **1962**, 84, 813-816.
- (44) Cook, D. *Can. J. Chem.* **1961**, 39, 1184-1189.
- (45) Bellamy, L. J.; Rogasch, P. E. *Spectrochim. Acta* **1960**, 16, 30-34.
- (46) Choo, J.; Lee, K. H.; Laane, J. *J. Mol. Struct.* **1996**, 376, 255-259.

- (47) Murray-Rust, P.; Glusker, J. P. *J. Am. Chem. Soc.* **1984**, *106*, 1018-1025.
- (48) Doronina, E. P.; Aksamentova, T. N.; Chipanina, N. N.; Mukha, S. A.; Medvedeva, S. A. *Russ. J. Gen. Chem.* **2009**, *79*, 297-302.
- (49) Lommerse, J. P. L.; Price, S. L.; Taylor, R. *J. Comput. Chem.* **1997**, *18*, 757-774.
- (50) Hazi, D. *J. Chem. Soc. (Resumed)* **1956**, 2725-2731.
- (51) Stevenson, F. J.; Goh, K. M. *Geochim. Cosmochim. Acta* **1971**, *35*, 471-483.
- (52) Starsinic, M.; Taylor, R. L.; Walker, P. L. Jr.; Painter, P. C. *Carbon* **1983**, *21*, 69-74.
- (53) Ishizaki, C.; Martí, I. *Carbon* **1981**, *19*, 409-412.
- (54) Cromwell, N. H.; Miller, F. A.; Johnson, A. R.; Frank, R. L.; Wallace, D. J. *J. Am. Chem. Soc.* **1949**, *71*, 3337-3342.
- (55) Moreno-Castilla, C.; López-Ramón, M. V.; Carrasco-Marín, F. *Carbon* **2000**, *38*, 1995-2001.
- (56) Painter, P. C.; Starsinic, M.; Squires, E.; Davis, A. *Fuel* **1983**, *62*, 742-744.
- (57) Fanning, P. E.; Vannice, M. A. *Carbon* **1993**, *31*, 721-730.
- (58) Brodskii, A. I.; Kotorlenko, L. A.; Samoilenko, S. A.; Pokhodenko, V. D. *J. Appl. Spectrosc.* **1971**, *14*, 633-638.
- (59) Ellis, G. P. In *Comprehensive Heterocyclic Chemistry: The Structure, Reactions, Synthesis and Uses of Heterocyclic Compounds*; Boulton, A. J.; McKillop, A., Eds.; Pergamon Press: Oxford, 1984; Vol. 3, pp 647-736.

(60) van der Marel, H. W.; Beutelspacher, H. *Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures*; Elsevier: Amsterdam, 1976.

(61) Kross, R. D.; Fassel, V. A.; Margoshes, M. *J. Am. Chem. Soc.* **1956**, 78, 1332-1335.

Table headings

Table 1. Chemical analyses of AC

Table 2. FT-IR spectrum of AC. Band positions and assignments

Captions to Figures

Figure 1. Chemical formulas of pyrones and chromenes: (I), 2-pyrone; (II), 4-pyrone; (III), 2H-chromene (2H-1-benzopyran); (IV), 4H-chromene (4H-1-benzopyran).

Figure 2. (V) Coumarin; (VI) Chromone-3-carboxylic acid.

Figure 3. FT-IR spectrum of AC between 4000 and 2000 cm^{-1} .

Figure 4. FT-IR spectrum of AC between 2000 and 400 cm^{-1} .

Table 1

Ash (% wt)	C (% wt)	H (% wt)	N (% wt)	S (% wt)	O (% wt)
4.72	86.50	0.51	0.26	0.64	7.37

Table 2

Spectral feature	Position/cm ⁻¹	Assignment ^a	Group/Structure
Peaks	3714, 3671, 3637	ν(O-H)	Phenol, inorganic matter
Shoulders	3452, 3315- 3129	ν(O-H)	Associated
Shoulder	3055	ν(C-H)	Aromatic ring
Shoulder	3025	ν(C-H)	Pyrone and chromene
Peaks	2972, 2883, 2823	ν(C-H)	2H-Chromene, 4H-chromene
		ν(O-H)	Quinone oximes
Band	1720	ν(C=O)	Pyrone, carboxylic acid
Shoulder	1657	ν(C=O)	4-Pyrone, quinone, ketone

Shoulder	1636	$\nu(\text{C}=\text{C})$	2-Pyrone, 4-pyrone 2H-Chromene, 4H-chromene
Band	1566	$\nu_s(\text{C}=\text{C})$ skeletal	Aromatic ring
		$\nu(\text{C}=\text{C})$	2-Pyrone
		$\nu(\text{C}=\text{N})$	Quinone monoxime
Shoulder	1470	$\nu(\text{C}=\text{C})$ skeletal	Aromatic ring
Shoulder	1442	$\nu(\text{C}=\text{C})$ skeletal	Aromatic ring
		$\delta(\text{CH}_2)$	Chromenes
		$\delta(\text{O}-\text{H})$	Quinone monoxime
Shoulder	1386, 1368	$\delta(\text{O}-\text{H})$	Phenol, carboxylic acid
Band	1279	$\delta(\text{O}-\text{H})-\nu(\text{C}-\text{O})$	Carboxylic acid
		$\nu_{as}(=\text{C}-\text{O}-\text{C})$	4H-Chromene
Shoulders	ca. 1249	$\nu_{as}(=\text{C}-\text{O}-\text{C})$	2H-Chromene, 2-pyrone
Shoulder	1209	$\nu(\text{C}-\text{OH})$	Phenol
Band	1166	Unassigned	Phenol
		$\nu(\text{C}-\text{C})$	4H-Chromene
Band	1114	Unassigned	Phenol, 2H-chromene
		$\delta(\text{C}-\text{H})$	2-Pyrone phenyl ring
Band	1069	$\nu_s(=\text{C}-\text{O}-\text{C})$	Aromatic ether
		$\nu(\text{N}-\text{O})$	Qinone oximes
		Unassigned	Quinone
Band	1024	$\nu_a(=\text{C}-\text{O}-\text{C})$	Aromatic ether
			2H-Chromene
			4H-Chromene

		$\nu(\text{N-O})$	Quinone oximes
Band	901	$\delta(\text{O-H}) +$ $\gamma(\text{OH}\dots\text{O})$	Carboxylic acid dimer
		$\nu(\text{C-O})$	4-Pyrone
Shoulder	868	$\gamma(\text{C-H})$	Tri- or higher substituted benzene ring
Shoulders	854, 816	$\gamma(\text{C-H})$	p-Disubstituted benzene ring
Shoulder	854	$\gamma(\text{O-H})$	Benzoquinone oxime
Shoulder	810	$\gamma(\text{C-H})$	m-Disubstituted benzene ring
Shoulder	794	$\gamma(\text{C-H})$	m-Disubstituted benzene ring
		$\delta(\text{C-H})$	2-Pyrone
		Unassigned	4-H-Chromene
Peak	740	$\gamma(\text{C-H})$	o-Disubstituted benzene ring Monosubstituted benzene rings
		$\delta(\text{C-H})$	2-Pyrone
		Unassigned	4-H-Chromene
Peak	702	$\gamma(\text{C-H})$	Monosubstituted aromatic ring
Peak	668	$\gamma(\text{C-H})$	Phenyl ring in 2-pyrone
Shoulder	625	$\delta(\text{C-H})$	2-Pyrone ring
Peak	564	$\gamma(\text{O-H})$	Associated
Peak	530	$\delta(\text{C=O}),$ inorganic matter	

^aAbbreviations: ν , stretching; δ , bending (in-plane); γ , bending (out-of-plane);

s, symmetric; as, asymmetric.

Figure 1

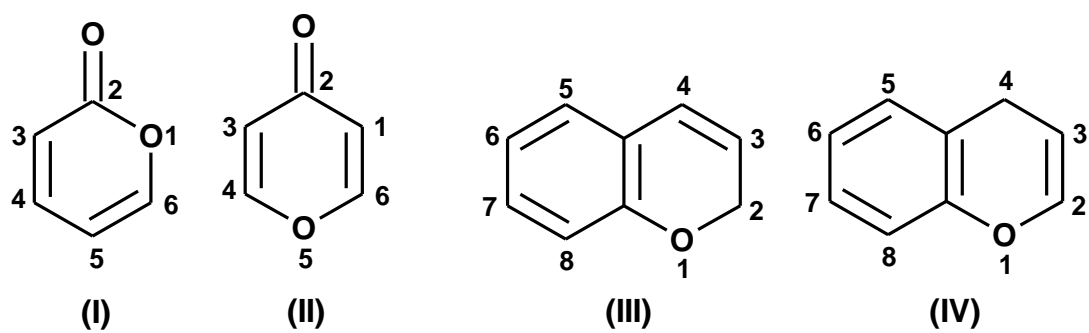


Figure 2

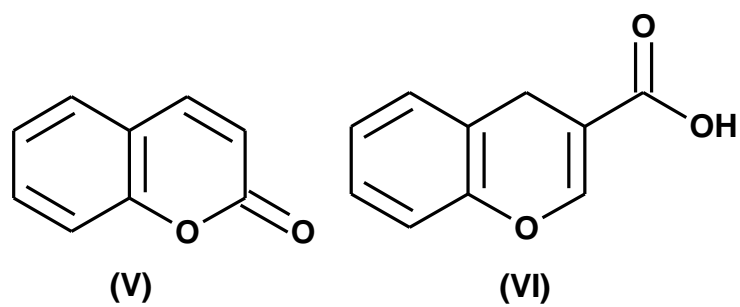


Figure 3

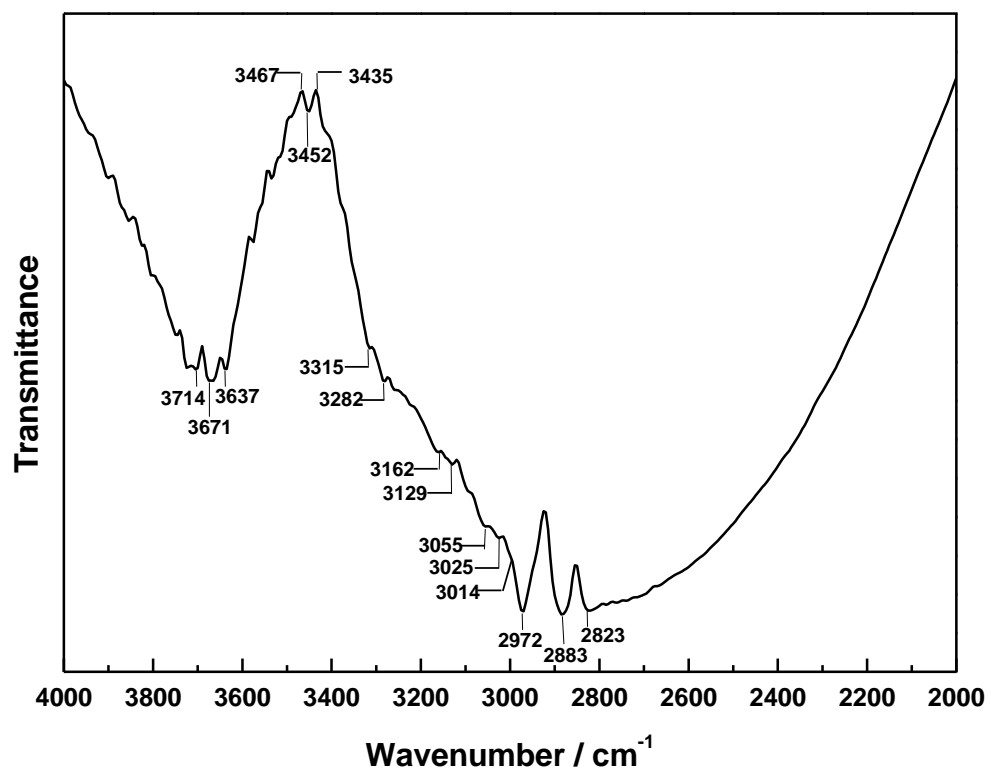


Figure 4

