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Basic Surface Oxides on Carbon Materials: A Global View

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Herein we report results from quantum chemical calculations on a large series of pyrone-like model compounds which are relevant for carbon basicity. In consonance with previous work (*Carbon* **1999**, *37*, 1002), pyrone-like functionalities at the edge of graphene layers are predicted to exhibit a broad range of pK_a values (4−13) depending on the relative position of the ketone and etheric rings. The thermodynamic stability of pyrones is discussed in terms of reaction energies calculated for selected isodesmic processes which give insight into the role of the adjacent basal plane, the relative abundance of polycyclic pyrone-like structures, and so forth. In addition, we show that hypothetical redox processes involving pyrone-like structures have estimated electrochemical potentials which lie in the range of those observed in many carbons. Finally, the ability of pyrone-like model compounds to provide a global view of the chemical and electrochemical properties of basic carbon surfaces is discussed.

Introduction

Most of carbon material applications involve interfacial interactions where different substances in the gas or liquid phase access the carbon surface.[1] The broad set comprising activated carbons constitutes a clear example of materials where the relevance of surface properties is essential.[2−4] For other carbon materials, carbon fibers for instance, the characteristics of their outermost layers play also a significant role in their primary applications (i.e., as reinforcement in composite materials).[5] As a result, considerable effort has been devoted to characterize and to comprehend the chemical properties of carbon surfaces, as well as their microstructure.

Carbon surface chemistry assumes traditionally the existence of a variety of surface complexes formed by combining carbon atoms with other elements (i.e., oxygen, nitrogen, hydrogen, and sulfur).[1] The accurate analytical description of the specific surface functional groups present on a given carbon material is infeasible. This inherent difficulty leads to a yet rather common situation where carbons are employed after empirical trial and error methods. On the other hand, overall surface properties related to the surface chemistry, such as the acid−base character or the redox properties, can be in most cases successfully determined experimentally. A desirable, next-coming scenario would encompass the connection of those properties with, at least, families of surface functionalities which are likely to exist in carbon materials.

Carbon surface oxides have been extensively investigated, since oxygen is the next most frequent element present in the surface of carbon materials. Oxygen atoms combine normally to carbon atoms, forming a wide spectrum of organic functionalities, from carboxylic acids to ketones and esters.[1,3] As has been just mentioned, these functionalities have been traditionally split into two families attending to their acidic or basic character in aqueous solution (see Scheme 1). There is general agreement about the type of surface functionalities that account for the acidic character of a carbon material (i.e., carboxyl groups, lactones, phenol and lactol groups). This is not the case for basic carbon surfaces, with several models of basic oxygen-containing functionalities being proposed: chromene structures,[6] diketone or quinone groups,[1,7] and pyrone-like groups.[3,8] There is no consensus about the strength as bases of these groups and the extent of their contribution to the overall carbon basicity. Moreover, there is some evidence that protons can be adsorbed on basal planes due to electrostatic interaction with the π electron system of the graphene structures.[9]

Carbons are also well-known for their ability to catalyze reactions involving the transfer of electrons between participating redox moieties. In this type of reactions, the carbon surface is able to donate or withdraw electrons from/to radicals or ion radicals that are expected to exist as stable species within graphene layers.[1] Furthermore, carbon materials can act as electrodes per se; that is, they exhibit redox activity when immersed in appropriate electrolytes. Many carbons thus exhibit electrochemical potentials that may be related to functional groups present in the outermost layers of the material. Hitherto, only two surface oxide complexes have been proposed to act as redox species: quinonoid-type groups and chromene groups (Scheme 2).[1] The fact that several carbons show electrochemical potentials in the range 0.6−0.8 V has

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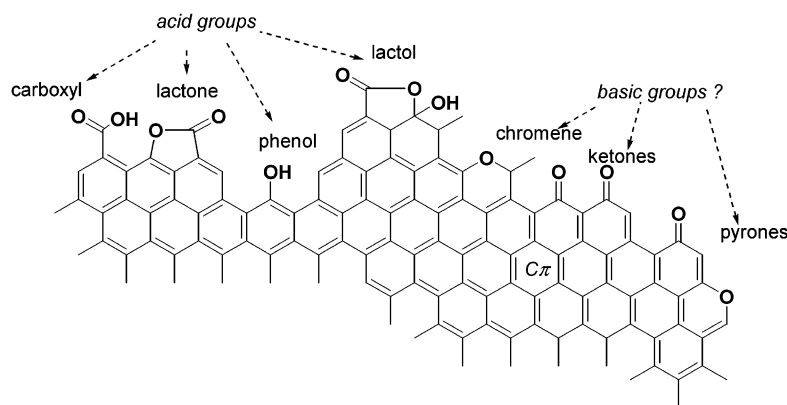
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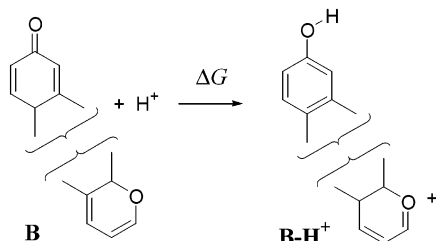(7) Contescu, A.; Vass, M.; Contescu, C.; Putyera, K.; Schwarz, J. A. *Carbon* **1998**, *36*, 247.

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Scheme 1

Scheme 2

strengthened the idea of hydroquinone groups (with E° between 0.5 and 0.7 V) being responsible of the redox activity in carbons. However, many other carbons exhibit a much wider range of electrochemical potentials (0−1 V).[1]

The pyrone-like structures, which are the basic surface oxides studied in this work, are combinations of non-neighboring carbonyl and ether oxygen atoms at the edges of a graphene layer, as originally defined by Voll and Boehm.[8] On carbon surfaces, the pyrone groups are supposed to be formed by air exposure of heat-treated carbons and to react as basic centers through acid−base reactions according to the Brønsted definition. As organic compounds, the *monocyclic γ-pyrones* are well-known organic compounds which exhibit a rather weak basicity ($pK_a \sim -1$). Thus, on the basis of the pK_a data of monocyclic pyrones, some authors have assumed a weak basicity of pyrone-like structures on carbon surfaces. However, we have recently shown using quantum chemical methods that *polycyclic* pyrones can cover a wide range of base strength (about 12 pK_a units).[10]

Clearly, an important base strength is required for pyrones to contribute to the overall carbon basicity. However, it is also clear that other requirements must be satisfied. For example, pyrones must be abundant on carbon surfaces. In other words, pyrones must be thermodynamically more stable than other plausible basic surfaces oxides. Herein we will provide some insight into the factors influencing the basicity, relative stability, and potential redox actvity of pyrones. First, we will examine the base strength in aqueous solution of the pyrone-like compounds by means of pK_a calculations on a large set of model compounds. Second, we will discuss the thermodynamic stability of pyrone-like groups embedded in polycyclic aromatic hydrocarbons on the basis of reaction energies of isodesmic processes.[11] These energetic calcula-

tions will allow us to ascertain the thermodynamic role of the adjacent basal plane, the relative stability of the polycyclic pyrone-like structures, and so forth. Finally, we will show that protonation of pyrone-like structures may trigger redox processes. Overall, the present contribution suggests that multiple combinations of sp² and sp³ oxygen atoms connected to graphene layers can provide a global description of the chemical and electrochemical properties of basic carbon surfaces.

Methods

pK_a Calculations. Model compounds were fully optimized at the HF/6-31G* and MP2/6-31G* levels of theory,[12] using the Gaussian98 suite of programs.[13] Electronic energies were then refined by carrying out single-point MP2/6-311+G(2d,2p) calculations on the MP2/6-31G* geometries. Thermodynamic data (298 K, 1 bar) were computed using HF/6-31G* analytical frequencies within the ideal gas, rigid rotor, and harmonic oscillator approximations.[14] To compute solvation energies ($\Delta G_{solvation}$), we used the united atom Hartree−Fock (UAHF) parametrization of the polarizable continuum model (PCM) including both electrostatic and nonelectrostatic solute−solvent interactions and simulating water as solvent.[15,16] This UAHF PCM reproduces the experimental solvation energies of 43 neutral molecules and 27 ions with errors of 0.2 and 1 kcal/mol on average for neutral solutes and ions, respectively. Thus, the solvation energies of the different structures were computed from single-point HF/6-31+G** PCM-UAHF calculations on the MP2/6-31G* gas-phase geometries.

The pK_a trend for a series of mono-, bi-, and tricyclic pyrone bases (**B**) with respect to a prototypical organic superbase (1,8-bis(dimethylamino)naphthalene, DMAN) was obtained by combining the MP2/6-311+G(2d,2p)// MP2/6-31G* gas-phase energies, the corresponding HF/

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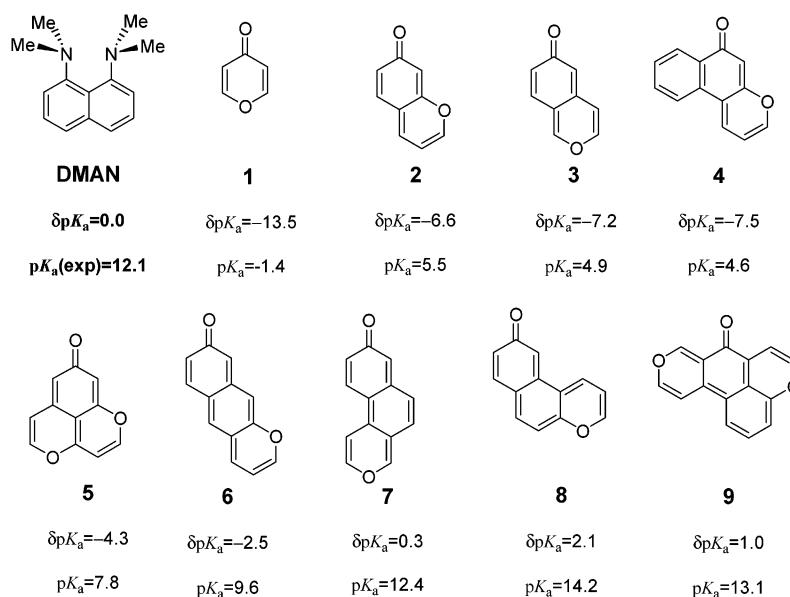(15) Barone, V.; Cossi, M.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3210.
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Scheme 3

6-31G* thermal corrections, and the solvation energies involved in the protonation process.

The pK_a of the **B**−**H**$^+$ species can be obtained using the following equation:

$$pK_a = -\Delta G/2.303RT$$

where

$$\Delta G = \Delta G_{\text{gas-phase}} + \Delta G_{\text{solvation}}(\mathbf{B}-\mathbf{H}^+) - \Delta G_{\text{solvation}}(\mathbf{B}) - \Delta G_{\text{solvation}}(\mathbf{H}^+)$$

Unfortunately, the agreement of ab initio pK_a determinations with experimental values is notoriously difficult, because very high levels of theory are required to accurately predict either the gas-phase components of proton affinities or the large solvation energies of ions, so that even small relative errors in the energy calculations can be very large on an absolute pK_a scale. In practice, only the estimation of relative pK_a's of related compounds can be done with confidence using quantum mechanical methods coupled with continuum models.

We note that, with respect to our previous calculations in ref 10, the computational procedure for obtaining the pK_a values reported in this work differs in (i) the theoretical method employed to compute the $\Delta G_{\text{solvation}}$ values, (ii) the nature of the acid−base reaction analyzed (B + H$_3$O$^+$ → B−H$^+$···H$_2$O in ref 9), and (iii) the identity of the reference compound (quinoline in ref 10).

Calculations of Reaction Energies: Isodesmic and Redox Processes. All the model compounds considered in the calculations of reaction energies were optimized at the HF/6-31G(d) level of theory. Subsequently, single-point MP2/6-31G(d) calculations were carried out on the HF/6-31G(d) geometries. We note that the MP2/6-31G-(d)//HF/6-31G(d) level of theory, whose computational cost increases moderately with the size of molecular systems, can make reasonable predictions of reaction energies for systems having closed shell reactants and products.[17] More specifically, even better agreement with experiment is found for *isodesmic* reactions, where the number of electron pairs and the number of bonds of each type are conserved.[11,12] For these processes, the electron correlation to a large extent is the same on both sides so that accurate values of reaction energies can be obtained at a rather low level of theory.

Results and Discussion

pK_a Calculations. Scheme 3 shows several pyrone-like model compounds and their relative pK_a's with respect to that of the 1,8-bis(dimethylamino)naphthalene (DMAN) (δpK_a values), as obtained computationally. By combining the δpK_a values with the experimental pK_a value of DMAN,[18] the absolute pK_a's for the series of pyrone-like compounds can be estimated. For the simplest monocyclic pyrone **1**, which has a very weak basic character, the predicted pK_a (−1.4) lies very close to the range of experimentally reported pK_a's (−1.14 < pK_a < 0.1), supporting thus our computational approach to estimate the relative pK_a's.

On going from the monocyclic pyrone **1** to the bicyclic structures **2**−**3**, the basic strength in aqueous solution is determined by two opposite factors. On one hand, the intrinsic basicity of **2**−**3** increases because their protonated forms are stabilized by conjugation throughout the etheric ring and the aromaticity of the resultant phenolic ring. For example, in terms of gas-phase free energies, the bicyclic pyrone **2** releases 230.5 kcal/mol upon protonation, 18.7 kcal/mol more than the monocyclic pyrone **1**. On the other hand, the increase in hydrophobic character with the number of aromatic rings fused and the larger delocalization of the global positive charge in the protonated forms attenuate solvent effects in stabilizing preferentially the protonated (basic) forms (these solvent effects, which are included in the $\Delta G_{\text{solvation}}(\mathbf{B}-\mathbf{H}^+)$ − $\Delta G_{\text{solvation}}(\mathbf{B})$ energy terms, disfavor the protonation of **2** with respect to **1** by 9.2 kcal/mol). Globally, the stabilization achieved by electronic conjugation dominates according to our calculations. Thus, the bicyclic pyrones **2** and **3** are stronger bases than **1** by ∼7 pK_a units with predicted pK_a values of 5.5 and 4.9, respectively.

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At the edges of an oxidized carbon surface, pyrone functionalities as **2** and **3** could be enlarged by adding either carbon rings or etheric rings. In this respect, our calculations show that substituent effects also affect the base strength of pryones. For example, when a carbon ring is fused with the bicyclic pyrone-like structure **2** to give model **4**, the predicted pK_a is slightly decreased by ~1 pK_a unit. However, inclusion of a second etheric ring as in the tricyclic structure **5** increases significantly the basicity by ~3 pK_a units with respect to **2**−**3**. When a carbon ring separates the carbonylic and etheric rings as in the tricyclic structures **6**−**8**, the computed pK_a values (>9) qualify them as strongly basic organic compounds. Note, however, that the exact pK_a of the tricyclic pyrones **6**−**8** is largely dependent on the position of the etheric ring. In particular, the pK_a of the strongest base compound **8** (14.2) is 2.1 units above that of the reference compound, the organic superbase DMAN. On the other hand, we also found that the simultaneous presence of etheric and carbon rings adjacent to a bicyclic pyrone can increase the basic strength, as in the case of the tetracyclic structure **9** with a predicted pK_a ~ 13.

Although the error bars in the computed pK_a may be still important (±1, ±2), the present and former pK_a calculations predict similar trends for the aqueous basicity of pyrone-like structures. Therefore, we conclude that our previous proposal that pyrone-like functionalities at the edge of graphene layers should exhibit a broad range of pK_a values is grounded on a firm theoretical basis regardless of the details of the theoretical models used.

Isodesmic Energies. As mentioned in the Introduction, the impact of the pyrone-like groups on the surface chemistry of carbon materials will be critically determined by their relative abundance and thermodynamic stability besides their intrinsic basicity. Owing to the lack of direct experimental information regarding the relative abundance of pyrones or other basic groups, we carried out theoretical calculations on adequately chosen isodesmic processes. An isodesmic reaction is usually a hypothetical (nonexisting in reality) chemical process in which the number of bonds of each formal type remains the same on each side of the equation but with changes occurring in their mutual relationships.[11,12] The energy changes (ΔE_{rxn}), which correspond to formal reactions, can reveal important trends in the relative stability of pyrones. For example, the **2** → **3** conversion between bicyclic pyrones is an isodesmic process with a reaction energy (ΔE_{rxn}) of only −1.3 kcal/mol at the MP2/6-31G(d)//HF/6-31G(d) level of theory. This small energy difference points out that the exact position of the etheric O atom can have only a weak impact on the thermodynamic stability of the *bicyclic* pyrone-like structures.

In general there are several possible ways of constructing formal isodesmic processes; that is, such methods are not unique. In this work, we adopted the bicyclic pyrone **2** as the reference compound from which the thermodynamic stability of other pyrones can be determined. Thus, the reaction energies connecting the bicyclic pyrone **2** into the tricyclic structures **6** and **8** are 9.2 and 18.0 kcal/mol, respectively (see Scheme 4). Similarly, the tetracyclic structures **10** and **11** are also less stable than **2** by 15.6 and 18.2 kcal/mol, respectively, according to the computed ΔE_{rxn} energies. These energy differences are quite large, and therefore, it is reasonably expected that bicyclic pyrone-like structures will be more abundant on carbon surfaces than the tri- and tetracyclic ones.

To obtain insight into the thermodynamic role of the adjacent basal plane on the stability of pyrone-like functionalities, we computed the reaction energies of the

Scheme 4
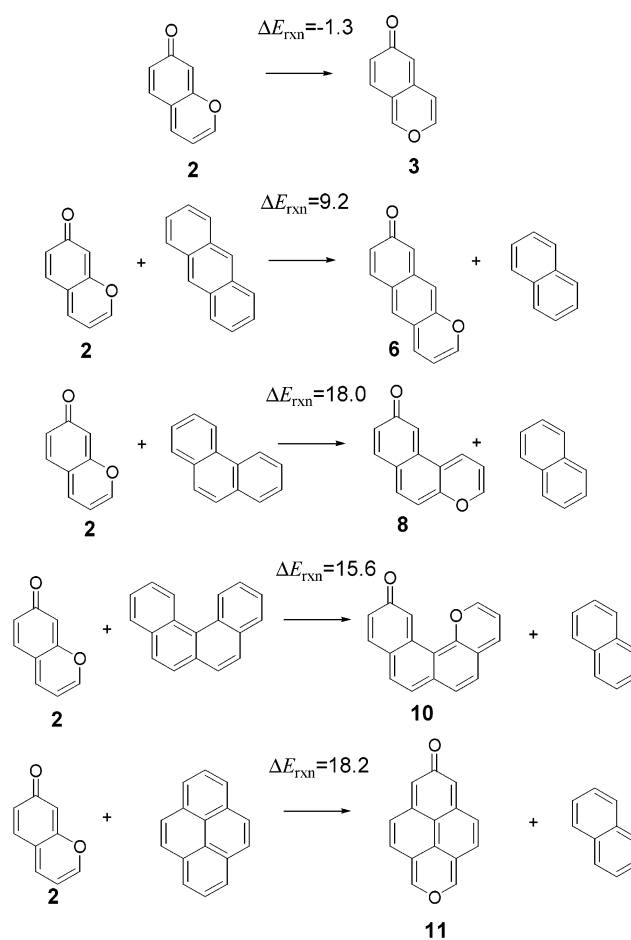
Scheme 5
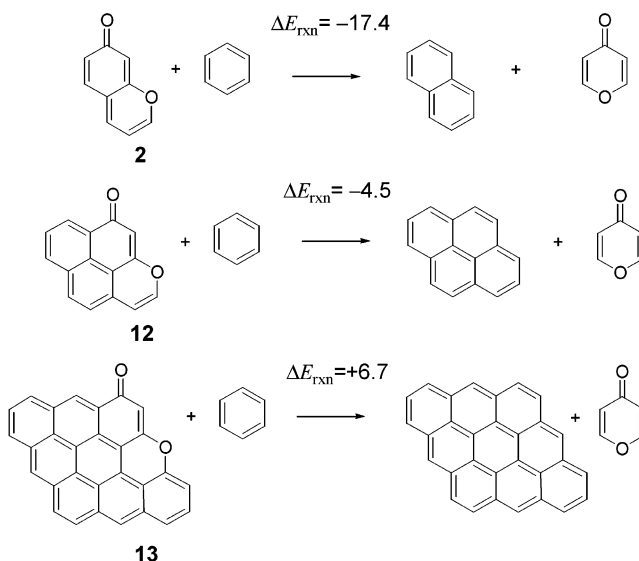
isodesmic processes shown in Scheme 5. These formal reactions reveal the impact of bicyclic pyrone-like groups on the electronic conjugation throughout the fused aromatic rings. For example, the pair of model compounds, anthracene + pyrone **1**, is much more stable than the pair benzene + pyrone **2** by 17.4 kcal/mol; that is, insertion of the carbonyl and etheric oxygen atoms within *two* aromatic rings disrupts the resonance stabilization and is energetically costly (first reaction in Scheme 5). However, this energetic penalty is mitigated and even removed when

Scheme 6

Scheme 7
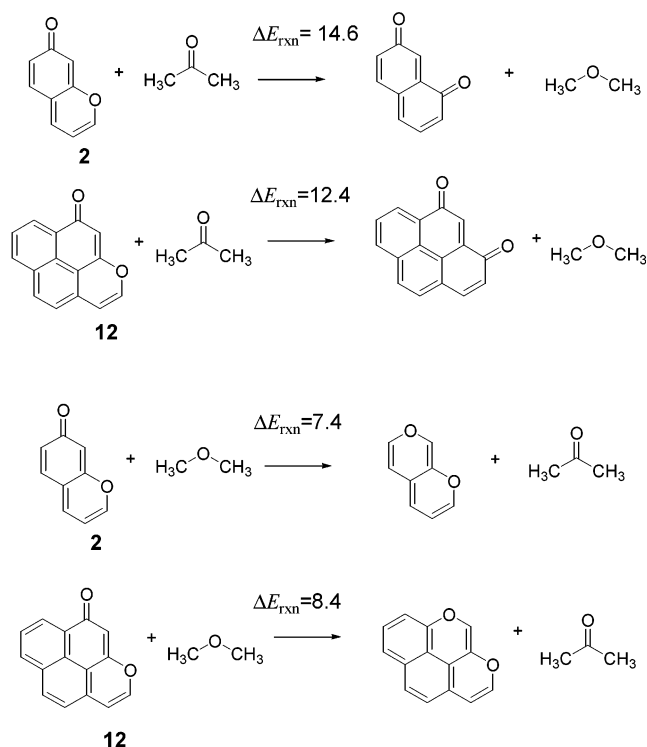
the bicyclic pyrone functionality decorates the edge of larger polycyclic hydrocarbons. In the case of the model compound **13**, the replacement of the pyrone group by an aromatic ring is energetically disfavored by 6.7 kca/mol; that is, insertion of bicyclic pyrone-like functionalities into *large* polycyclic hydrocarbons is thermodynamically favored with respect to that into small aromatic molecules.

The key structural feature of pyrone-like functionalities is the combination of sp^2 (carbonylic) oxygen and sp^3 (etheric) oxygen atoms whereas other possible surface oxides on carbon surfaces present either all-sp^3 oxygens (i.e., chromenes) or all-sp^2 oxygens (diketones, quinones). Thus, one may wonder whether a mixture of sp^2/sp^3 O atoms at the edge of graphene layers is more stable or not than a population of all-sp^2 O atoms (or all-sp^3). In this respect, examination of the isodesmic energies in Scheme 6 indicates that the simultaneous presence of sp^2 and sp^3 O atoms (i.e., pyrones) leads to the most stable structures when two oxygen atoms are included in two adjacent rings. Although many other situations could be examined by means of these and other isodesmic processes (e.g., other diketone structures, tricyclic and tetracyclic pyrones, etc.), it is much more likely that the mixture of sp^2 (exocyclic carbonyls) and sp^3 (cyclic ethers) O atoms would remain as thermodynamically favored. Nonetheless, we also note that the exact balance between sp^2 and sp^3 O atoms would depend on the previous history of the carbon material (e.g., oxidation conditions of the heat-treated carbon surfaces, the structure and reactivity of C atoms with free valences at the edge of graphene layers, etc.).

Proton Binding and Simultaneous Redox Processes. Solid carbons can undergo redox processes under appropriate experimental conditions. As mentioned in the Introduction, quinonoid basic groups or chromenes (see Scheme 1) are thought to be responsible for this redox activity.[1] However, we speculate that pyrone-like groups could accept electrons upon protonation on the carbonylic O atom so that the net reduction process shown in Scheme 7 might occur.
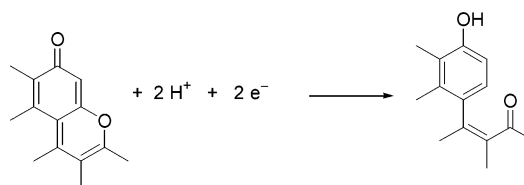
In this hypothetical half-reaction, the conjugated carbonyl group is reduced to phenol while the reduction of the heterocycle leads to its ring opening with formation of a new conjugated carbonyl group. To find out if this process is thermodynamically feasible, we calculated the reaction energy for the reduction of the bicyclic pyrones **2**, **12**, **13**, and **14** relative to that of anthraquinone, which can be considered as a representative of quinonoid structures on carbon surfaces (see Scheme 8). We found that reduction of the smallest pyrone **2** is thermodynamically much easier than reduction of anthraquinone, as shown by the computed reaction energy −25.9 kcal/mol at the MP2/6-31G(d)/HF/6-31G(d) level. This exoergicity most likely stems from the aromaticity gained in the resultant phenolic ring. For the larger pyrone structures **12** and **13**, their relative reducing ability is substantially weakened given that the reaction energies are now endoergic by 1.4 (**12**) and 33.0 kcal/mol (**13**). This effect can be understood in terms of the equilibrium geometry of the reduced forms of **12** and **13** (see Figure 1). While the reduced form of **12** is still a planar molecule, the most stable reduced form of **13** is *nonplanar* due to the geometric constraints imposed by the large number of fused rings (see structures **12** and **13(nonplanar)** in Figure 1). Of course, the loss of planarity of pyrones upon reduction hinders the electron conjugation throughout the fused rings. To further clarify the nature of these geometrical effects, we also optimized a *planar* structure of the reduced form of **13** which turns out to be 8.7 kcal/mol *less* stable than the nonplanar one. Thus, we see in Figure 1 that this planar structure is destabilized by a strained C−C−C angle (∼130 °) and a too short C−H···O hydrogen bond contact (1.61 Å). However, the steric effects depend largely on the exact disposition of the carbonyl and etheric rings. For example, reduction of the model system **14**, in which the pyrone rings are embedded in an irregular polyaromatic system, is more favorable by 1.1 kcal/mol than that of anthraquinone. On the other hand, we also considered a *tricyclic* pyrone model (**15** in Scheme 9) which resembles an *armchair* configuration. The relative reducing ability of **15** turned out to be much larger than that of anthraquinone ($\Delta E_{rxn} = -55.4$ kcal/mol), owing to the large aromaticity gained upon reduction without substantially altering the planarity of the conjugated rings (see Figure 1). Overall, we conclude that, from the point of view of thermodynamics, pyrone-like groups on carbon surfaces could be considered as reducible species when either the etheric ring of pyrones is not fused with three carbon rings or the etheric ring and the basal plane are arranged in an armchair configuration (Scheme 9).

The energetic trends outlined in Scheme 8 can be expressed in terms of reduction potentials if we approximate the standard free energies $\Delta G°$ by the computed electronic energies ΔE_{rxn}. By using the Nernst relation ($\Delta G° = -zFE°$) and the standard reduction potential $E°$ for the anthraquinone semisystem (0.13 V), the approximate $E°$ values for **2**, **12**, **13**, **14**, and **15** are 0.69, 0.10, −0.58, 0.15, and 1.1 V, respectively. We note that the estimated $E°$ potentials of **2**, **12**, **14**, and **15** lie in the
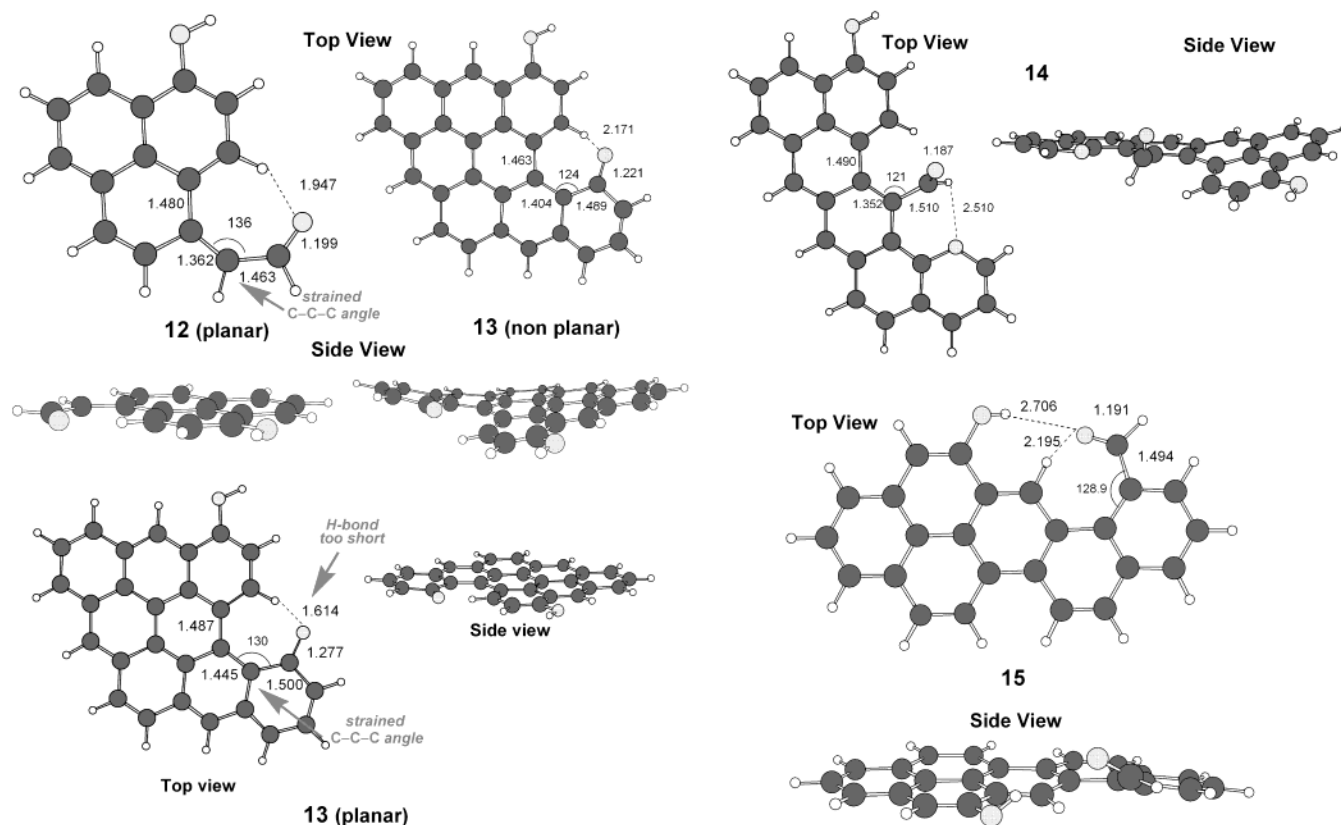
Scheme 8
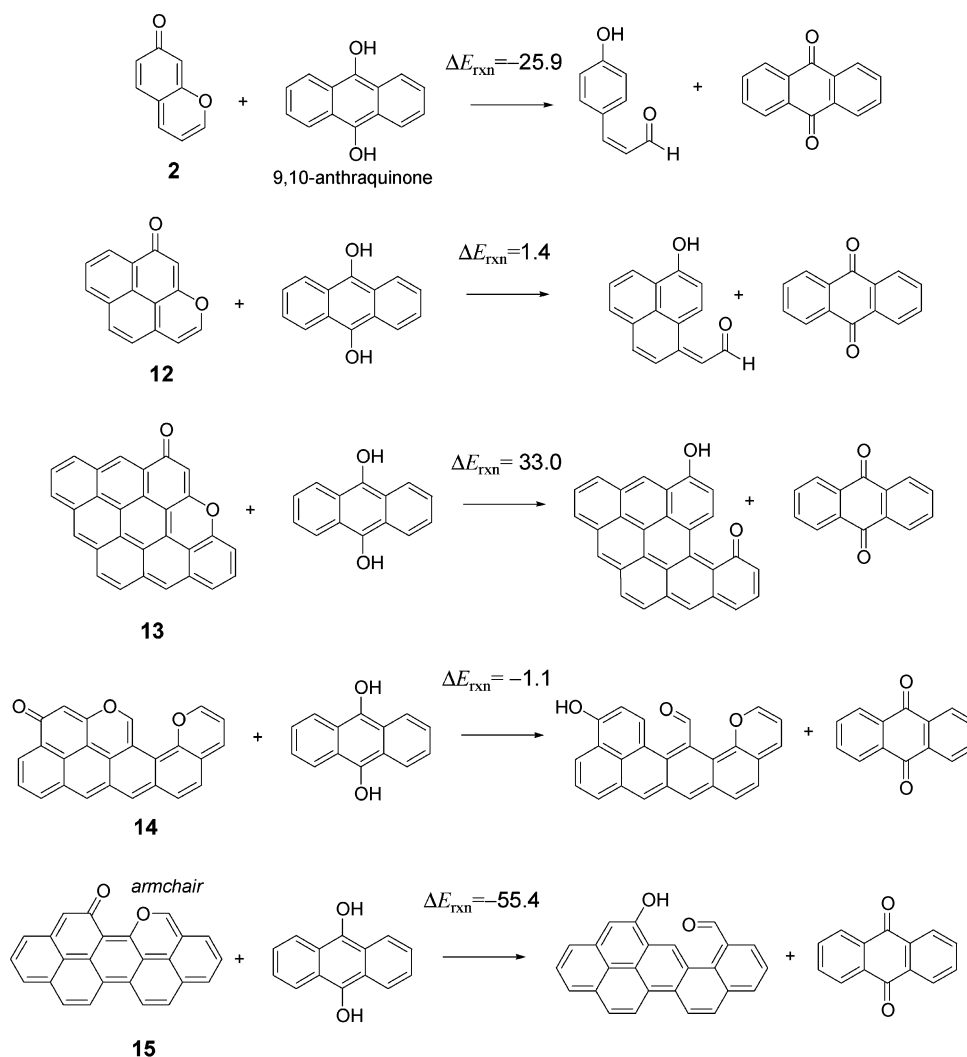
range of electrochemical potentials observed in many carbons (0−1 V), supporting thus the proposed participation of pyrone-like groups in the redox activity of carbon surfaces.

Global View on Basic Surface Oxides on Carbon Materials. According to previous proposals, the formation of basic surface oxides on carbon surfaces may occur as follows: Heat treatment generates active sites (free valence C atoms) at the periphery of graphene layers by decomposition of carboxylic acid, lactone, and phenol groups. Upon cooling in an inert atmosphere and reexposure to air, oxygen becomes fixed. In this scenario pyrones appear by a combination of etheric O atoms and carbonyl groups. These hypotheses about the origin of pyrones have now a firmer basis thanks to our computational results. Thus, the isodesmic energies above-discussed point out that, in effect, oxidation of carbon surfaces to a *mixture* of sp^2 and sp^3 O atoms attached to carbon is thermodynamically more favorable than oxidation to either all-sp^2 or all-sp^3 O atoms. We also found that *bicyclic* pyrones would be especially stable structures, with the adjacent basal plane further contributing to stabilize them. The fact that each pyrone group occupies a large space (at least two carbon rings) is in consonance with the measured surface coverage of carbon blacks by basic groups (~2 nm^2).[19]

After having assessed the relative stability of pyrone-like structures, we consider their role as organic bases. The present and former calculations clearly indicate that protonation on the carbonylic O atom is greatly favored by electronic conjugation throughout the carbon skeleton of polycyclic pyrones. The computed pK_a's (5−6 for structures **2−3**, ~8 for structure **5**, and 10−13 for **6−9**) explain well the continuous pK_a distribution observed in an activated basic carbon. This theoretical pK_a assignment is in good agreement with experimental proton binding isotherms which show that the most important proton binding processes occur in the ranges of pK_a 4−7, 8.4−8.6, and >9.5.

In addition to their acid−base chemistry, basic surface oxides in carbon materials might be involved in surface redox processes. We propose that, in the presence of reductive species, protonation of pyrone-like structures would be the first step in a surface reduction process which converts the original carbonyl group into a phenol group while the etheric ring may suffer a reductive cleavage which in turn generates a *new* carbonyl group. This hypothetical half-reaction, which corresponds to a 2H$^+$/2e$^−$ process such as that of the quinone/hydroquinone pair (see Scheme 7), would be a specific reaction of pyrones. The transfer of two electrons agrees well with redox processes observed most commonly in voltammetry experiments of carbons.[1] To our knowledge, there are no reported data about organic reduction processes similar

(19) Papirer, E.; Li, S.; Donnet, J.-B. *Carbon* **1987**, *25*, 243.

Figure 1. HF/6-31G* optimized structure of the postulated reduced forms of the pyrones **12**, **13** (planar and nonplanar), **14**, and **15**.

Scheme 9
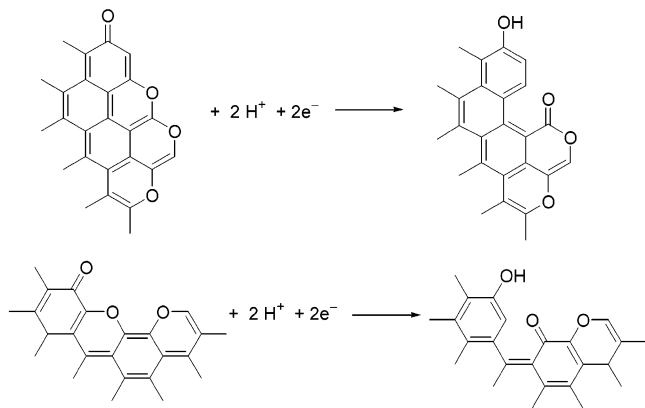
to the proposed reductive cleavage of the etheric rings in conjugated systems apart from the cleavage of allyl aryl, vinyl aryl, and benzylic ethers by strong reducing agents such as AlH(*i*-Bu)$_2$.[20] However, it is also clear that further theoretical and experimental work would be needed to further clarify this point.

Finally, we note that "pyrones as acid−base and redox centers" constitutes an attractive and plausible hypothesis that could help us clarify some questions regarding carbon basicity. For example, it has been reported that the number of basic groups on a carbon surface does not necessarily correlate with the number of carbonyl groups, as observed by Papirer et al.[19] This fact can be well understood in terms of "pyrones as reducible species" given that the number of basic groups on a carbon surface will not be limited by the O-sp^2/O-sp^3 ratio. In other words, a carbon surface with many more etheric rings than carbonyl groups could correspond to a basic carbon, since the protonation → reduction process of one pyrone functionality would regenerate one carbonyl group that could be adjacent to other etheric rings, creating thus a new pyrone group. This self-generating ability of pyrones on a carbon surface richer in O-sp^3 than in O-sp^2 is represented in Scheme 9: two different pyrone semisystems react, leading to a new pyrone and a lactone group. Moreover, the hypothetical reductive processes shown in Scheme 9 strongly suggest that the basicity and redox activity of carbon surfaces would be mainly determined by the *global* distribution of peripheral etheric and carbonyl rings rather than *specific* functional groups.

(20) Smith, M. B.; March, J. *March's Advanced Organic Chemistry: Reactions, Mechanism and Structure,* 5th ed.; Wiley-Interscience: New York, 2001.