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INFLUENCE OF ACTIVATED CARBONS TEXTURAL PROPERTIES ON ACETAMINOPHEN ADSORPTION AT DIFFERENT TEMPERATURES

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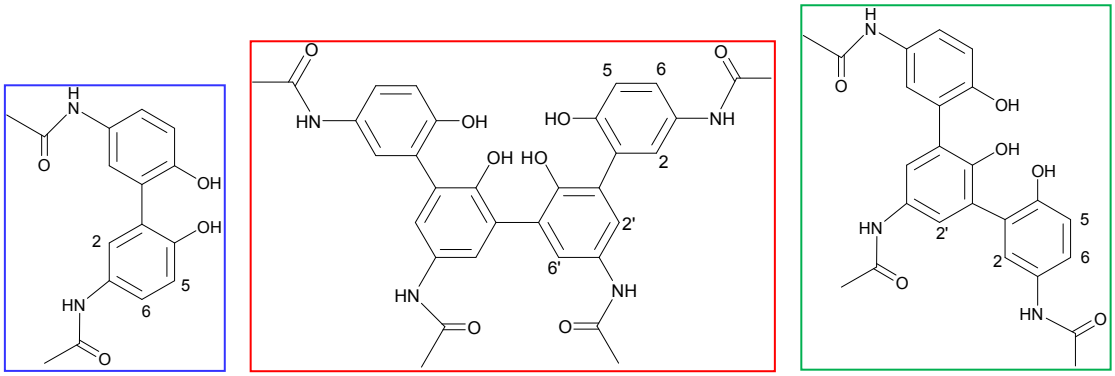
Supporting Information

^{1}H NMR results



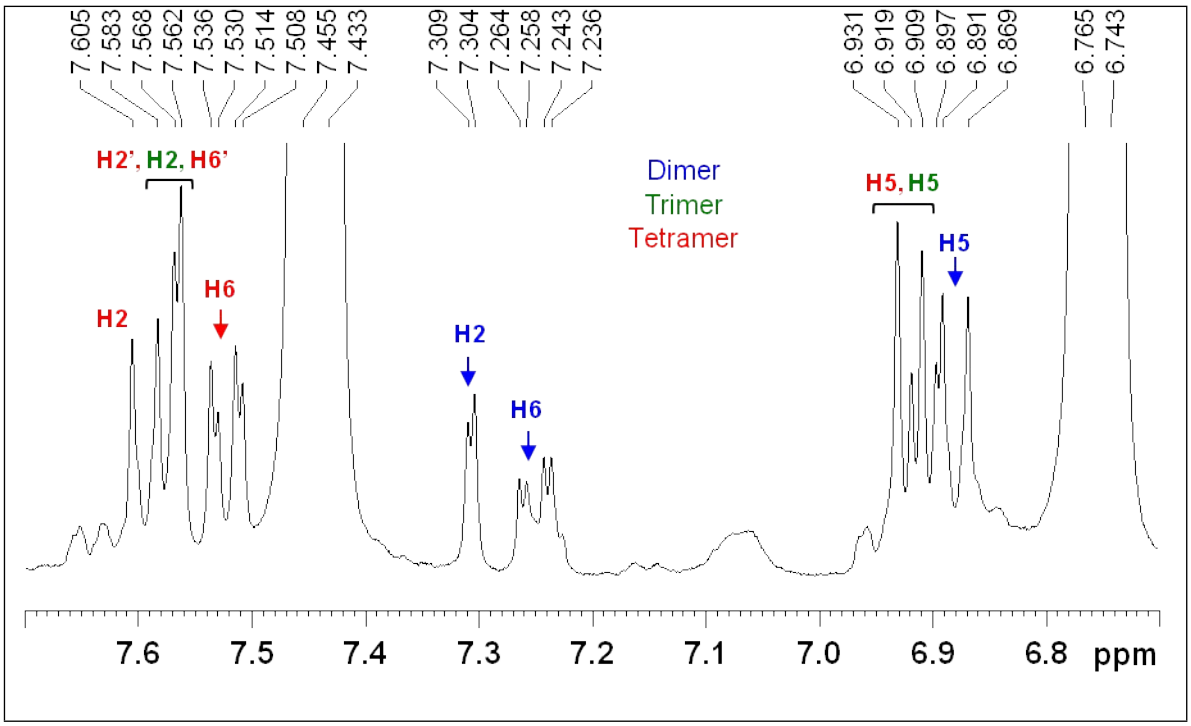


Fig. S1. Schematic representation of the oligomers with atom labels and 1H NMR spectrum (400,13 MHz) of the aromatic region in acetone-d6 (with the intensity scale highly amplified to enhance the minor products signals).

The acetaminophen monomer can easily be identified in the ^{1}H NMR spectrum displayed in Figure S1 trough the two high intensity doublets at 7.44 and 6.75 ppm

(J= 8.8 Hz). However, the minor peaks observed in the spectrum indicate the presence of distinct related compounds, though at much lower concentration.

Unfortunately, additional 1D and 2D NMR spectra such as ^{13}C, COSY, HSQC and HMBC were not helpful because the relevant peaks were obscured by noise due to the close proximity of the intense resonances of the acetaminophen monomer. Hence, the present NMR analysis is mainly based on the relationship between the actual results and those reported by Potter et al.[49].

In fact, the resonance patterns and chemical shifts observed in this proton spectrum closely resemble those reported by Potter et al.[49], for symmetric acetaminophen oligomers in which the monomers are linked through the carbon atoms adjacent to the hydroxyl groups (Fig. S1), namely the dimer, the tetramer and, eventually, the trimer. Analysis of the lower chemical shift region displayed, suggests the presence of three species. Though partially overlapped, three doublets can be recognized at 6.92, 6.91 and 6.88 ppm, with identical coupling constants (J=8.8 Hz), consistent with *ortho*-coupling of aromatic protons (with no *meta*-coupling). Their lower frequency is in accordance with the shielding effect usually observed for aromatic protons *ortho* to OH substituents and these features are in agreement with the existence of three distinct H5-type protons.

Admitting that the relative sequence of the proton chemical shifts for the three compounds in acetone-d6 is similar to that observed in dmso-d6 by Potter et al. [49], the more shielded doublet (6.88 ppm, J=8.8 Hz) corresponds to the proton H-5 of the dimer, which is correlated to the doublet of doublets (dd) at 7.25 ppm (J=8.8 and 2.4 Hz), assigned to its *ortho*-coupled proton H-6 which in turn is *meta*-coupled to H-2 at 7.307 ppm (d, J=2.3 Hz).

The splitting patterns and coupling constants expected for the additional oligomers are basically similar to those observed for the dimer, except that an additional signal is

expected for the trimer and two additional peaks for the tetramer. Their potential identification, which is pointed in the spectrum (Figure S1), was also performed by analogy with the corresponding spectra found in Potter's work. Some peaks of the trimer are apparently missing, probably due to overlap by the monomer signal close by or even by some resonance of the tetramer.

It should be noted that some *meta*-coupled resonances are not resolved, appearing as broad singlets instead.

Molecular dimensions of the low energy conformation of acetaminophen tetramer

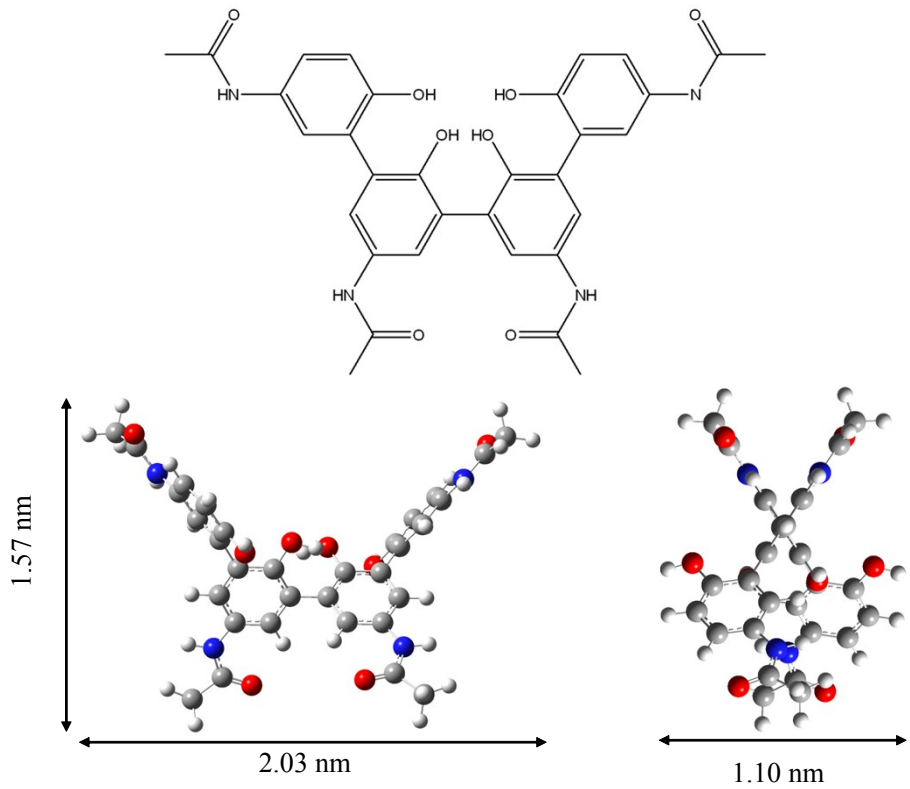


Fig. S2. Molecular dimensions of the low energy conformation of acetaminophen tetramer (oxygen in red, nitrogen in blue, carbon in gray, and hydrogen in white).

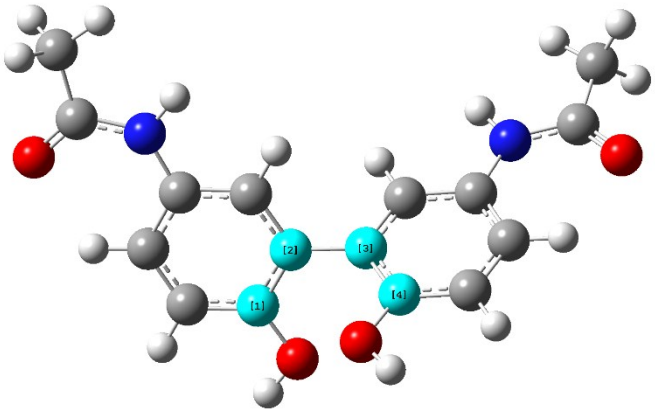


Fig. S3. Molecular structure of acetaminophen dimer with the atoms that define the dihedral angle highlighted in blue (atoms 1-4).

Calculation of the internal energy change due to temperature increase

In the following some theoretical calculus are detailed aiming an ease understanding of the discussion made to explain the different acetaminophen adsorption temperature dependence onto microporous activated carbons. All the calculus considered took into account the dimer structure presented in Fig. S3.

Change in internal energy can be estimated from the heat capacity at constant volume (C_v) using the thermodynamic relation:

$$\Delta U = C_v \Delta T \quad (1)$$

Since there is no tabulated C_v values for the acetaminophen dimer and its determination would be very difficult since it would be required to obtain the dimer in pure form, the C_v was estimated from computational methods (see section 2.4), at a reference temperature of 25ºC. In equation 1 it is assumed that the C_v value is constant within the temperature interval, which is a reasonable assumption for this relatively small interval.

Estimation of the population change of the dimer conformations due to temperature increase

The temperature increase in the system will permit a higher number of molecules to access the energy states above the ground state (lower energy conformation). In the present case, this means that the temperature increase will allow an increase in the number of molecules with conformations corresponding to angles between monomers more apart from the most stable angle. We are thus interested to understand if such an increase is significant in confirmations that can access the majority of the micropores in the activated carbons Pi-fa/800 and Pi-fa/900. The energy change due to the change in the dihedral angle between monomers (using the low energy conformation as reference) can be related to the ratio between the number of molecules in the high and ground state, considering the Boltzman distribution:

$$\frac{N_i}{N_0} = e^{-[(\Delta E)/k_B T]} \qquad (2)$$

where N_i and N_0 are the number of molecules in state i and ground state, respectively, ΔE is the energy difference between the state i and the ground state, k_B is the Boltzman constant and T is the temperature of the system. From equation 2, the population distribution can be obtained for 20 and 40ºC using the energy profile of the different dimer conformation considering the rotation between two monomers. This will give the population distribution for the dihedral angle rotation at the two temperatures.

Since we are more interested in understanding the variation of the distribution with temperature rather than the distribution itself, we calculated the population change between the distribution at 20 and 40ºC, and plotted the results as a function of the angle change (Fig. S2). The results show that the magnitude of the changes is small

(< 0.05%) and that the highest increase is seen at 15, 115, 210 and 280º rotation. This increases occurs at expenses of the number of molecules at lower energy conformations (0, 130, 195, 295º rotation). The conformations were a more significant increase was observed have critical dimensions of 0.60 and 0.63 nm and, considering the micropore size distributions of the activated carbons Pi-fa/800 and Pi-fa/900 (Fig. S2), the increase in the accessible pore volume for adsorption is not significant. Thus, the observed increase in adsorbed amounts on these samples cannot be justified simply by the change in distribution of conformations of the dimer with temperature.

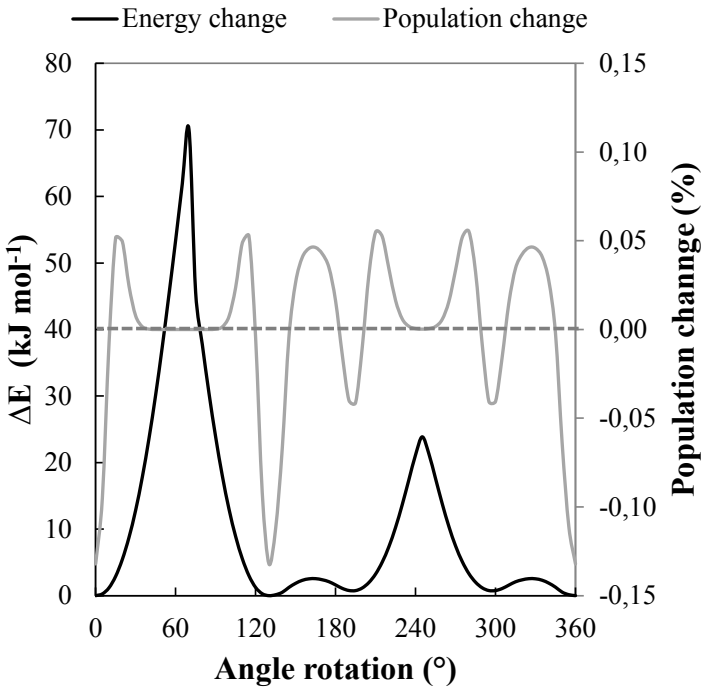


Fig. S4. Energy profile of the different dimer conformation, considering the rotation between two monomers and the respective population change for each conformation due to the temperature increase from 20 to 40 ºC.

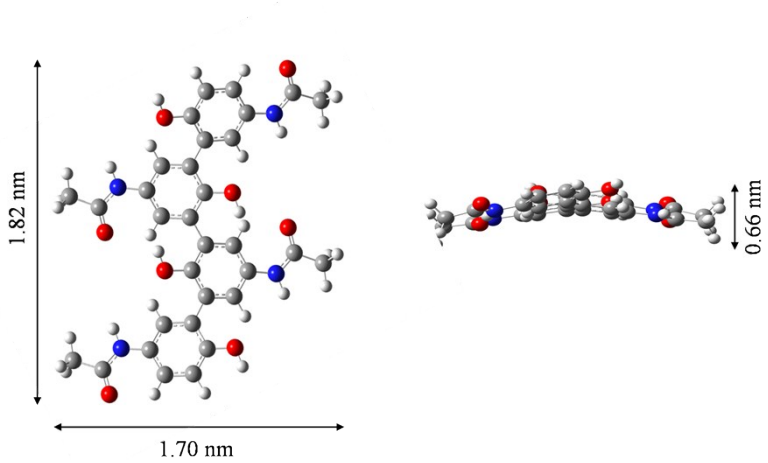


Fig. S5. Molecular dimensions of the conformation of acetaminophen tetramer with dihedral angles identical to those of conformation C and D of the dimer shown in the text (oxygen in red, nitrogen in blue, carbon in gray, and hydrogen in white). The completely planar form has a critical dimension similar to that of the dimer and monomer.