

**Elucidating the structure of light absorbing styrene
carbocation species formed within zeolites**

SUPPORTING INFORMATION

S1. Computational Details

Styrene derivatives such as pure styrene (Sty), 4-fluorostyrene (4-FSty), 4-chlorostyrene (4-ClSty), 4-bromostyrene (4-BrSty), 4-methylstyrene (4-MeSty) and 4-methoxystyrene (4-MeOSty) were studied. Ground state structures of the molecules were obtained by means of Density Functional Theory (DFT) calculations. The optimized geometry for each compound was obtained using the hybrid meta GGA density functional M06-2X¹ with the 6-31+G(d,p) standard basis set. All harmonic vibrational frequencies were real; therefore the structures are minima on the potential energy surface.

Proton affinity (PA) was calculated for the styrene substituted monomers. It is defined as the negative values of the enthalpy process of protonation at 298.15 K: $PA = -\Delta H_{BH^+}(298.15K)$, for the chemical reaction $B + H^+ \rightarrow BH^+$, where B is a chemical compound with available electrons that reacts with H^+ to form the protonated species BH^+ . The reaction to calculate PA for styrenes derivatives is shown in Figure S1.

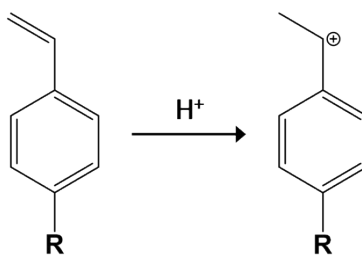


Figure S1. Protonation reaction of styrene derivatives for the calculation of proton affinities.

Time dependent (TD)-DFT excited states calculations of singlet–singlet transitions were carried out with the M06-2X functional and with the 6-31+G(d,p) standard basis set. The accuracy of this approach to predict the experimental UV-Vis spectra was recently

studied for protonated thiophene-based oligomers². The ground state geometries were employed throughout all excited state calculations. Thus, the theoretical excitation energies correspond to vertical transitions, which can be approximately identified as absorption band maxima in experimental absorption spectra.

Aromaticity studies were conducted by three different indexes. Nucleus-Independent Chemical Shifts (NICS)³ values were calculated for the optimized geometries at M06-2X/6-31+G(d,p) level of theory using the continuous set of the gauge transformation method. Because the NICS values are distant dependent, the ghost atoms were placed on the geometrical center of each benzene ring ($z = 0$ or 1). Another structure-based index of aromaticity, the so-called harmonic oscillator model of aromaticity (HOMA) index was used. Its definition is:

$$HOMA = 1 - \alpha/n \sum (R_{opt} - R_{ij})^2$$

where n is the number of bonds taken into summation and α is an empirical constant fixed in a way to give HOMA = 0 for a Kekulé structure of the typical aromatic system and equal to 1 for the system with all bonds equal to the optimal value R_{opt} .⁴ Bird index is another geometrical-based quantity to describe aromaticity and it is based upon a statistical evaluation of the extent of variation of ring bond order provided by the expression^{5,6}:

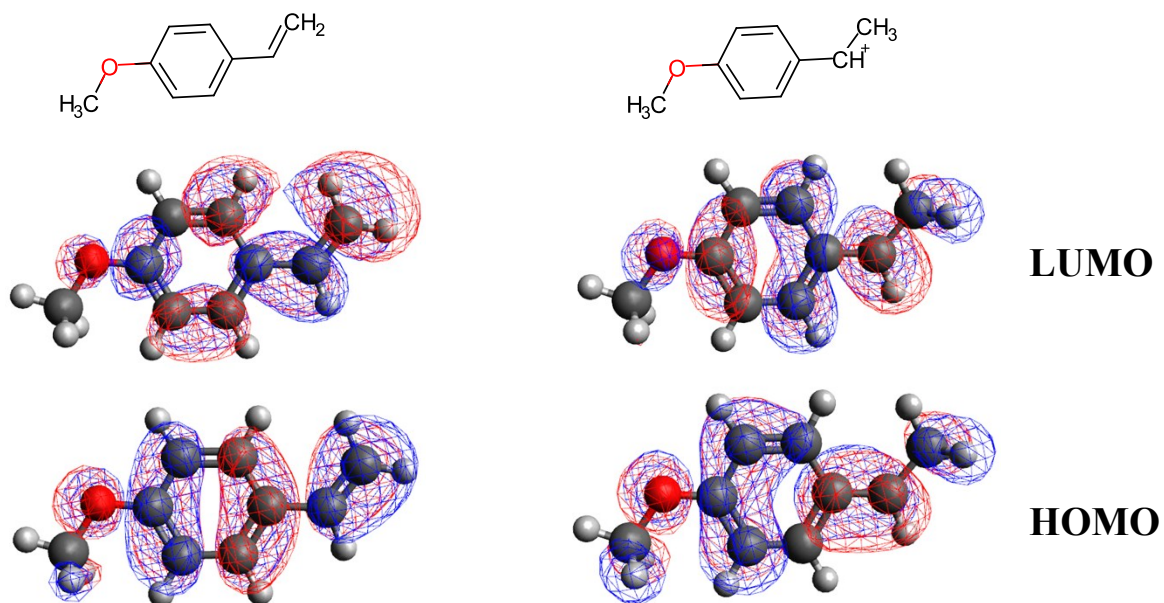
$$I_A = 100 \left(1 - \frac{V}{V_K} \right), \quad \text{where} \quad V = \frac{100}{N} \sqrt{\frac{\sum (N_{ij} - N)^2}{n}}$$

N is the arithmetic mean of the n various ring bond orders, N_{ij} , which are obtained experimentally. V_K is the value of V for the corresponding non-delocalized form of the ring. The more the Bird index is close to 100, the stronger the aromaticity is.

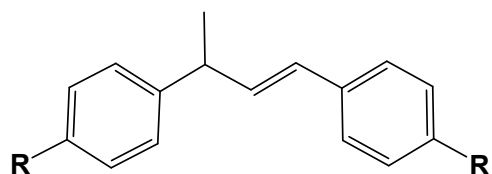
The quantum theory of atoms in molecules (QTAIM)⁷ was used to study the properties of the C-C bond between the protonated C atom and the C atom on the aromatic ring as a Bond Critical Point (BCP). This C-C bond was fully characterized by their topological properties such as the Laplacian of the electron density (L), ellipticity (ϵ), electron localization function (ELF) and the Laplacian bond order.⁸

The calculations of geometry optimization, vibration analysis, TD-DFT and NICS were performed with the Gaussian 09 software⁹. QTAIM and aromaticity studies were carried out in the Multifunctional Wavefunction Analyzer (Multiwfn) developed by Tian Lu and Feiwu Chen¹⁰.

S2. Frontier MOs of 4-methoxystyrene monomers



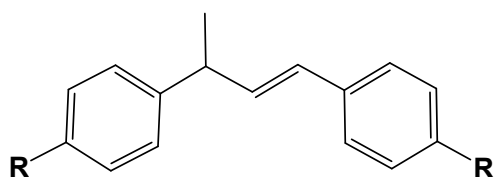
S3. Aromaticity indexes for the unsaturated neutral dimeric compounds.



R

H	-7.87	-7.25
F	-9.67	-9.12
Cl	-8.46	-7.79
Br	-8.40	-7.67
Me	-7.95	-7.39
MeO	-9.08	-8.22

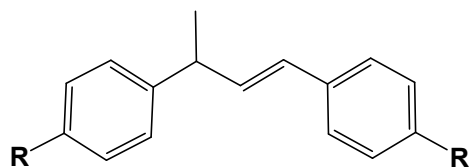
Fig S2. NICS (0) values for neutral unsaturated dimer species with different substituents.



R

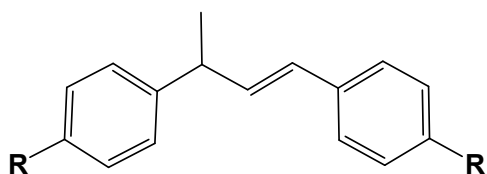
H	-10.53	-9.88
F	-10.64	-10.21
Cl	-10.24	-9.73
Br	-10.10	-9.64
Me	-10.27	-9.98
MeO	-10.43	-9.84

Fig S3. NICS (1) values for neutral unsaturated dimer species with different substituents.



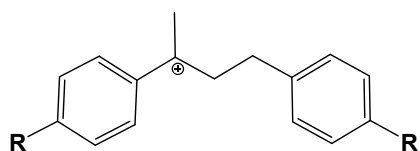
R		
H	0.99	0.98
F	0.99	0.98
Cl	0.99	0.98
Br	0.99	0.98
Me	0.98	0.97
MeO	0.98	0.97

Fig S4. HOMA values for neutral unsaturated dimer species with different substituents.

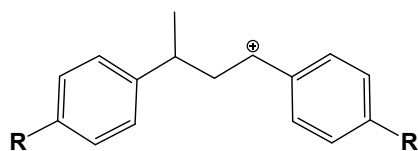


R		
H	98.33	96.22
F	95.75	94.39
Cl	97.67	95.75
Br	97.70	95.51
Me	97.26	95.72
MeO	96.42	93.85

Fig S5. Bird aromaticity index for neutral unsaturated dimer species with different substituents.



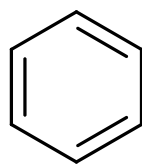
R		
H	-3.91	-7.83
F	-4.76	-9.50
Cl	-3.61	-8.20
Br	-3.39	-8.08
Me	-3.33	-7.89
MeO	-2.80	-8.73



R		
H	-7.80	-3.33
F	-9.50	-4.09
Cl	-8.13	-2.98
Br	-8.01	-2.83
Me	-7.88	-2.67
MeO	-8.63	-2.98

Fig S6. NICS (0) values of benzene rings. Left side: ternary carbocation species and right side: secondary carbocation species.

Figure S7. Aromaticity indexes for benzene at M06-2X/6-31+G(d,p)



NICS(0)	-7.73
NICS(1)	-10.60
HOMA	0.99
Bird	99.96

S4. Cyclic carbocation species (5)

The electron properties for the cyclic carbocation species (5) are shown in Table S1. The position of the absorption band has the same trend due to the substituent group. The proposed structure for this compounds in previous works for 4-MeOSty has been based on the isolation of a neutral cyclic species with an absorption band at 490 nm. The calculated λ in this study (455 nm) agrees with this value. On the other hand, the band for 4-FSty or the other styrene-based compounds have never been confirmed experimentally, for 4-FSty this band in this theoretical study is located at 392 nm. It means that one can expect its possible formation within zeolites and its absorption band must be blue shifted with respect to 4-MeOSty.

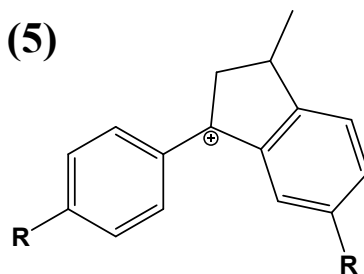


Table S2. Electronic properties of cyclic protonated species. Energies of the frontier orbitals, main absorption wavelength (λ) and dipole moment (μ).

Compound	ϵ_{HOMO} (eV)	ϵ_{LUMO} (eV)	$\Delta\epsilon_{\text{H-L}}$ (eV)	λ (nm)	μ (D)
Sty	-12,08	-6,68	5,40	368	0.06
4-FSty	-12,05	-6,92	5,13	392	3.68
4-ClSty	-11,75	-6,91	4,84	415	4.62
4-BrSty	-11,50	-6,88	4,62	436	6.68
4-MeSty	-11,54	-6,42	5,12	390	0.43
4-MeOSty	-10,78	-6,19	4,59	455	2.27

S5. References

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