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1 Introduction

Chemical moieties substituting H atoms of benzene and larger aromatic rings are generally known to have significant effects on the chemical properties of the aromatic compounds, through their ability to either withdraw or donate electrons to the π -conjugated system.¹ Substituents already present on the aromatic ring behave, for example, as activating/deactivating as well as positional selectivity factors in electrophilic and nucleophilic aromatic substitution (EAS and NAS, respectively) reactions.^{2,3} These observations triggered the birth of an area of study of the relationships between structure and aromatic

Competition between electron-donor and electron-acceptor substituents in nitrotoluene isomers: a photoelectron spectroscopy and *ab initio* investigation[†]

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We present an investigation of the close relationship between chemical structure, physical properties and reactivity of the three nitrotoluene isomers: a joint experimental and theoretical study, based on X-ray photoelectron spectroscopy (XPS) measurements and *ab initio* calculations, addressing the complex interplay between the competing electron-donor and electron-acceptor effects of the nitro- and methyl-substituents on the chemical properties of the nitrotoluene isomers. As the main results of the investigation we: (i) point out that accurate *ab initio* calculations play a key role in the complete assignment of photoemission measurements, as well as in the estimate of proton affinities in the case of all the eligible sites; (ii) revisit, at a more quantitative level, textbook models based on inductive and resonant effects of different substituents of the aromatic ring, as well as on the hyper-conjugative connection of the methyl group to the π -conjugated system; (iii) provide an accurate analysis of correlation patterns between calculated proton affinities and core-ionization energies, which represent a powerful tool, capable of predicting site-specific reactivities of polysubstituted molecules in the case of electrophilic aromatic substitution reactions.

properties.⁴ Early theoretical investigations of structure-properties correlations in substituted benzenes were focused on the displacements of the ground-state valence electronic density at given molecular sites.⁵ Core-ionization energies (IEs), measured by X-ray photoelectron spectroscopy (XPS), represent a more direct probe of the ability of aromatic molecules to accept positive charge at a specific site, as they are related in a strict quantitative way to the screening of photoinduced core holes by means of the displacement of the valence electronic density in a positively charged ionized state.^{6,7} The addition of H⁺ ions to the same molecules by means of proton transfer processes, in which aromatic compounds act as Brønsted bases, introduces an alternative class of positively charged intermediates. The proton affinity (PA) of different molecular sites, regulating the formation of different protonated species, represents the key quantity of such processes.8 PA estimates are pivotal in understanding concepts and processes such as proton-coupled electron transfer reactions, acidity and alkalinity of organic molecules, and kinetics of EAS reactions. Reliable information of PAs is therefore intrinsically valuable.

A fruitful relationship has been established between the above two classes of positively charged aromatic molecules: several studies have reported patterns of linear correlations between protonation enthalpies and IEs, and deviations from

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Paper

these linear patterns have been used to identify preferential sites of electrophilic attack to the aromatic ring. The occurrence of such a linear correlation has been long established in the case of N(1s) and O(1s) XPS measurements.9-20 It has been shown recently that the same holds in the case of C(1s).²¹⁻²³ However, there are practical limitations to the experimental evaluation of PA; protonation enthalpy values can be measured only for the most favorable protonation sites of each molecule.8,23 On the other hand, IEs can, in principle, be measured for all the atoms of the molecule, even if accidentally degenerate lines, especially in the case of polysubstituted benzene rings, can be grouped into unresolved broad peaks. These experimental limitations can be overcome by performing accurate theoretical ab initio estimates of PA values and XPS lines, univocally assigned to all the eligible sites, which can be used to draw correlations patterns between PA and XPS data.

In this scenario, nitroaromatic compounds have been selected in order to shed light on different facets of the above structure-properties relationship. They are relatively rare in nature, but widely used in the chemical industry for the production of dyes, resins, pesticides, herbicides, explosives, and other useful materials.²⁴⁻²⁶ In particular, we focus here on the three nitrotoluene isomers, both because of their usage as starting reactants or intermediates in a large number of technologically relevant synthesis processes, and because of the concurrent presence of competing substituents on the aromatic ring. More specifically, we present the first in-depth experimental and theoretical investigation of C(1s) IEs and PAs of such compounds, aimed at elucidating how their electronic and chemical properties are influenced by the presence of the two competing electron-donor methyl and electron-attracting nitro groups.1 The different relative positions on the benzene ring of the CH₃ and NO₂ moieties play a crucial role in the electronic and chemical properties of the nitrotoluene compounds, thus offering a significant benchmark for testing whether IE and PA estimates can be used to foresee and elucidate chemical quantities such as reaction rates in EAS processes.² The results obtained allow quantitative predictions of the activation of different molecular sites, e.g., in the case of further nitration of several CH3- and NO2-substituted rings.27 Moreover, a detailed comparison between experimental measurements and theoretical calculations, including the screening effects of core holes, provides a deeper understanding of the electronic properties of substituted aromatic compounds, e.g., the study on a quantitative basis of the positional selectivity induced by the conjugation of the methyl group to the benzene ring,4,28,29 in agreement with the textbook hyper-conjugation model.1

Further effects of the competition of CH_3 and NO_2 groups on the electronic properties of nitrotoluene isomers have been investigated by performing experimental photoelectron measurements of the O(1s) and N(1s) shells, and in the spectral region of valence electrons, and by comparing the results with the properties of molecular orbitals, as described by *ab initio* calculations. Such investigations provide direct information on molecular orbital changes due to the displacement of conjugated electrons, as well as additional proofs of the activation/ deactivation effect of aromatic substituents on the benzene ring. In order to provide a full account of the nitrotoluene investigation, these additional measurements and calculations have all been reported in the ESI.[†]

2 Experimental and computational details

XPS spectra have been measured at the gas phase photoemission beamline of the ELETTRA synchrotron radiation source (Trieste, Italy)30 using a commercial 6-channels, 150 mm hemispherical electron energy VG analyzer, and the same setup which has been described previously.6 The three nitrotoluene isomers were obtained from Sigma-Aldrich with a minimum purity of 99% and used without any further purification. The ortho- and meta-nitrotoluene isomers are liquids under standard conditions, with a vapour pressure sufficiently high for the present experiment. The para-nitrotoluene isomer forms yellow crystals and requires moderate heating of the gas inlet system to 313 K to obtain the same target density, avoiding the decomposition of the sample. The XPS spectra were calibrated using a mixture of the molecule under investigation and of a calibration gas with well-known XPS lines in the same IE range, that is, CO₂ (C(1s) at 297.7 eV).³¹

Theoretical values of vertical XPS C(1s) IE have been calculated by means of *ab initio* density functional theory (DFT) methods in a supercell approach, as implemented in the Quantum-ESPRESSO package.32 Equilibrium geometries have been found by fully relaxing all the molecules accommodated in large cubic supercells (25 $Å^3$) to minimize the occurrence of spurious interactions between periodically replicated images. Total energies have been calculated by using norm-conserving Troullier-Martins atomic pseudopotentials,33 a plane-wave basis set, and the B3LYP hybrid exchange-correlation functional.34,35 Satisfactorily converged results have been achieved by using cutoffs of 80 Ry on the plane waves and of 320 Ry on the electronic density, respectively, as well as the Γ point for the k-point sampling of the Brillouin zone. H(1s), C(2s) and (2p), N(2s) and (2p), and O(2s) and (2p) electrons have been treated as valence electrons. All of the inner shells are embedded in the pseudopotentials. C(1s) XPS chemical shifts have been estimated by total energy differences between "standard" and "core-hole" calculations.6,36 In the latter case, an excited state C pseudopotential containing a 1s core hole has been used in place of the regular pseudopotential. A different calculation has been performed for each nonequivalent C atom. The energy differences between the standard and core-hole calculations have been compared with the corresponding difference obtained for the C atom of a CO2 molecule, accommodated in every supercell and used as a reference for both the theoretical and experimental chemical shifts. Despite the fact that the above theoretical framework is not often used to investigate the properties of isolated molecules, it provides very accurate predictions of C(1s) XPS IEs: differences between experimental measurements and theoretical estimates not exceeding the value of about ± 0.1 eV have been reported in the case of halogenated pyrimidines, where all the XPS lines could be assigned to given atoms.6

Moreover, this kind of calculation is easily scalable with comparable accuracy to larger molecules and molecule–surface interacting systems.³⁷

Theoretical calculations of PA have been performed by using the Gaussian 03 package.³⁸ Optimized geometries have been obtained by means of DFT calculations, performed using the B3LYP functional and a localized $6-311G^{++}(d,p)$ basis set. Stable molecular structures have been obtained, in full agreement with the above plane-wave based calculations. Moreover, proton affinities have been estimated by calculating protonation enthalpy values. Such values have been calculated using a refinement of the well established procedure proposed by Maksić *et al.*^{8,39,40} In this theoretical approach, PAs are calculated employing the general equation.

$$PA(B_{\alpha}) = (\Delta E_{el})_{\alpha} + (\Delta ZPE_{\nu})_{\alpha}$$
(1)

where $(\Delta E_{\rm el})_{\alpha} = [E(B) - E(BH)_{\alpha}^{+}]$ and $(\Delta ZPE_{\nu})_{\alpha} = [ZPE(B) - E(B)_{\alpha}^{+}]$ $\text{ZPE}(BH)_{\alpha}{}^{+}]$ are the electronic and the zero-point vibrational energy (ZPE) contributions to the PA, respectively. Here, B and BH⁺ denote the molecule and its positively charged conjugate acid, respectively, and α indicates the site of proton attack. The method has been widely applied with a surprising success to a large variety of polysubstituted benzenes and naphthalenes by using a MP2(fc)/6-31G**//HF/6-31G* + ZPE (HF/6-31G*) setup, which indicates that the ZPE was estimated at the HF/6-31G* level multiplied by a common empirical factor 0.89.40 The results are generally in good agreement with measured values; however, qualitatively wrong PA values have been calculated in the case of this setup when applied to strongly deactivating groups such as NO₂, NO and CN.⁴¹ For these reason, the PAs presented in this work have been obtained by using the G3B3 approach.42 G3B3 is an accurate, composite method for the calculation of the energies of molecules containing first and second row elements. It is based on the G3 method⁴³ which uses geometries optimized at the MP2(FU)/6-31G* level and scaled HF/6-31G* zero point energies, followed by a series of single point energy calculations as well as spin orbit and high level corrections. The G3B3 method is identical except that it is based on B3LYP/6-31G* geometries and scaled B3LYP/6-31G* zero point energies.

3 Results and discussion

As introduced above, C(1s) core level spectra, assisted by parallel theoretical estimates, give access to a deeper understanding of electronic properties as well as of chemical properties, *e.g.*, reactivity in EAS reactions, in the case of poly-substituted benzene rings such as the nitrotoluene isomers. The presence of competing electron-donor and -attractor groups such as CH₃ and NO₂, respectively, together with highly accurate experimental and theoretical estimates of C(1s) core shifts, represents a fruitful chance to reach the heart of well-established text-book models. These models, describing the inductive and resonant effects of benzene substituents, the activation/deactivation of the chemical reactivity of a given molecular position, the hyperconjugation of the CH₃ group with the benzene ring, can be accounted for at a more quantitative level. From this point of view, a close relationship between collected experimental measurements and two different kinds of theoretical estimates, the former related to core shifts, the latter concerning PA of unsubstituted C sites of the benzene ring, will be discussed in the following.

3.1 Fine analysis of C(1s) ionization energy values

The C(1s) core-level spectra of the ortho-, meta- and para-nitrotoluene isomers measured at a photon energy of 382 eV are shown in Fig. 1 together with the results of the theoretical predictions. The spectra have been measured with an overall energy resolution of 0.32 eV, mainly determined by the energy resolution of the electron analyzer. Carbon dioxide, whose binding energy, vibrational structure and natural width are well known,44 has been mixed with the molecule under investigation to calibrate the binding energy scale as well as to estimate the energy resolution of the present spectra. In the XPS measurements, the core ionization of each inequivalent C atom produces a distinct profile in the C(1s) spectrum.45 With respect to the benzene ring where all the C atoms are equivalent, the inequivalent C sites of the three isomers of the nitrotoluene molecules result in bands shifted by different amounts, due to the position and effect of the concurrent methyl and nitro groups, and composed by different peaks related to the vibrational structure which characterize the different core-ionized states. In o- and m-nitrotoluene all of the seven C atoms are formally inequivalent, while in the case of the *p*-isomer there are only five inequivalent C atoms: the methyl C0, the C1, C4, C2/C6 and C3/C5 atoms (see Fig. 1 and Table 1). The present XPS spectra are measured about 95 eV above the ionization threshold. In such conditions, the expected post collisional interaction (PCI) energy shift of a typical C(1s) state of lifetime Γ ≈ 0.10 eV is less than 0.013 eV,^{46,47} *i.e.*, negligible with respect to the present energy resolution. However the lineshape, being affected by an undefined number of overlapping and unresolved vibrational progressions, may be different from one state to another. A fitting procedure of the spectra would require a complete series of 7, 7, and 5 bands in the ortho-, meta- and para-nitrotoluene cases, respectively. Independent of the lineshapes, which can be represented by simple asymmetric Gaussian functions,6 as well as by more accurate convolution of theoretically calculated vibrational contributions to the ionized state,23 a procedure which leaves all the fitting parameters as free variables would result in strongly correlated parameters, leading to a representation of the spectrum which is far from being "unique". Hence, no assignment of the C(1s) IE values can be achieved on the grounds of the measurements alone. It requires an accurate theoretical analysis which takes into account the chemical shifts, as reported in Table 1. However some qualitative observations can be done by looking at the XPS spectra in Fig. 1. They show two broad asymmetrical bands, the low-energy one (A in Fig. 1) with a distinct shoulder (B) in the case of the o-nitrotoluene. All the peaks are shifted to higher IE with respect to those of toluene, due to the well known, strong electron attracting ability of the NO₂ group. In particular, the



Fig. 1 C(1s) XPS spectra of o-nitrotoluene (a), *m*-nitrotoluene (b), and *p*-nitrotoluene (c). Experimental measurements (open circles) have been fitted with Gaussian lineshapes (full black lines). The spectra have been measured at a photon energy of 382 eV with an overall resolution of 0.32 eV. The labels A–C indicate the main features of the spectra, also reported in Table 1 and discussed in the text. Dashed lines represent convolutions of Gaussian peaks centered on the 0–6 bars (0–4 in the case of *para*-nitrotoluene), corresponding to the theoretical estimates of C(1s) XPS lines for the C0–C6 carbon atoms, also reported in Table 1.

shifts are significantly pronounced (1.5 eV) for C atoms directly bonded to the nitro-group. The bands at higher energies, centred around 291.8 eV (C), are therefore easily attributed to the ionization of the C2, C3, and C4 positions of the *o*-, *m*-, and *p*-nitrotoluene isomers, respectively. Table 1XPS C(1s) and PA values. IE values corresponding to the mainfeatures of XPS spectra (labeled A-C in Fig. 1) are compared withcalculated C(1s) ionization energy values related to the three nitro-toluene isomers, reported together with proton affinity values

Measured			Calculated	
Peak	IE (eV)	Atom	IE (eV)	PA (eV)
o-Nitrotol	uene			
A	290.8	C6	290.61	-7.38
		C4	290.66	-7.42
		C5	290.76	-7.30
		C3	290.78	-7.25
		CO	290.82	_
В	291.2	C1	291.15	_
С	291.8	C2	291.75	—
<i>m</i> -Nitroto	luene			
Α	290.8	C6	290.68	-7.38
		C2	290.71	-7.35
		C4	290.75	-7.42
		C5	290.79	-7.30
		C1	290.97	_
		C0	291.08	_
С	291.8	C3	291.81	_
<i>p</i> -Nitrotol	uene			
A	290.8	C2,6	290.75	-7.35
		C3,5	290.93	-7.17
		C1	291.08	_
		C0	291.20	_
С	291.7	C4	291.79	—

Calculated XPS C(1s) values are represented by numbered bars below the spectra in Fig. 1, while the corresponding Gaussian convolutions by the dashed lines above the spectra. An overall good agreement between the shapes of the experimental and theoretical spectra is observed. We exploit this close agreement between theoretical and experimental data to attempt a first analysis of the present results on the grounds of calculated IE values. We employ, at a more quantitative level, an elementary model based on the interplay between the stronger, isotropic inductive (I) effects and the weaker, anisotropic resonant (R) effects, both contributing to the screening of photoinduced C(1s) core holes. The former are related to the electronegativity of the substituting groups and affect both the whole molecule, with global charge density withdrawal from, or donation to the aromatic system, and every single atom, the nearer the atom to the substituting group, the stronger the effect. The latter are conventionally ascribed to the extension of π -conjugation to the substituents, and are generally interpreted by using resonance structures in which positive charges are anisotropically shared between different sites of the π -conjugated network of bonds. The I-R model has been often used to illustrate the properties of substituents in aromatic compounds because it provides an intuitive and powerful tool to understand and predict the results of relevant classes of chemical processes such as the EAS reactions.^{1,2} This simple, two-contribution model has been applied in the present investigation to a different kind of positively charged system, in order to provide a

fine analysis of the screening of a core hole, by using IEs as the leading quantities. Moreover, the I-R model is generally extended to non-conjugated groups bonded to aromatic rings, e.g., the CH₃ moiety investigated in the present work, through the hyper-conjugation effect.^{4,23,28,29} This effect is described as the formation of a π -like overlap between the true aromatic conjugated system and an almost vertical sp³ σ orbital belonging to a non-conjugated substituent, inducing a partial delocalization of the σ charge density on the aromatic ring (a detailed description of the hyper-conjugative effect involving the CH₃ moiety is provided in Section 3.2). This, in turn, allows one to analyze in a unified framework the effects of the CH₃ and NO_2 groups on the C(1s) IEs of the nitrotoluene isomers. We anticipate here the existence of a close relationship between two different kinds of positively charged state, *i.e.*, the reaction intermediate of EAS (σ complex) and the ionized molecule carrying a C(1s) core hole; this relationship will be discussed in more detail in Section 3.3.

The calculated IE values of benzene, toluene, nitrobenzene, and the three nitrotoluene isomers, together with I and R effects of the CH₃ and NO₂ groups, which can both stabilize (–) and destabilize (+) a positive charge, have been displayed in Fig. 2 to favor the cross-comparison of data. As previously shown in the case of CH₃- and F-polysubstituted benzene rings,^{22,23} the effects of multiple substituents on the C(1s) IEs can be effectively described in terms of an additivity model. In detail, each energy shift Δ (IE) with respect to the benzene value (290.37 eV) is considered to be the sum of independent effects of the individual substituents.⁴⁸ In the case of toluene, nitrobenzene, and the three nitrotoluene isomers, this corresponds to a simple expression $\Delta(IE) = \sum_{i} n_i \alpha_i + m_i \beta_i$ where the α_i and β_i parameters represent the effects of *ipso*, *ortho*, *meta* and *para* substitutions of the n_i methyl and m_i nitro groups on the IE values, respectively. This expression is well fit by the calculated values shown in Fig. 2. The best fit α_i and β_i parameters have been reported in Table 2. First of all, as mentioned above, the large electron-withdrawing behavior of the NO₂ group dominates the charge density distribution of nitrobenzene and nitrotoluenes; a generalized and consistent blue shift of all the C(1s) IEs of nitrotoluenes with respect to those of benzene is indeed found, which is responsible for a significant deactivation of

Table 2 XPS C(1s) and PA additivity parameters. Additivity parameters for the effect of CH₃ and NO₂ substitutions on the C(1s) vertical ionization energies and on enthalpies of protonation of C sites. All the values are in eV

		Ionization energies	IE std error ^a	Enthalpies of protonation	EP std error ^a
CH ₂	inso	0.15	0.04	_	_
0113	ortho	-0.21	0.04	-0.31	0.02
	meta	-0.11	0.04	-0.19	0.02
	para	-0.18	0.04	-0.37	0.03
NO_2	ipso	1.59	0.04	_	_
	ortho	0.60	0.03	0.72	0.02
	meta	0.52	0.03	0.71	0.02
	para	0.55	0.04	0.74	0.03

^{*a*} Standard errors (SE) have been calculated as SE = (95% confidence interval)/2a where the *a* parameter depends on the number of degrees of freedom of the fit; *a* = 2.1199 (*a* = 2.2281) in the case ionization energies (enthalpies of protonation).



Fig. 2 Theoretical estimates of vertical C(1s) XPS lines (black values) and of protonation enthalpies (magenta values) of benzene, toluene, nitrobenzene, and of the three nitrotoluene isomers, all reported as negative or positive shift with respect to the benzene values. Positive weak (+) and strong (++), as well as negative (-) inductive (I) and resonant (R) effects on the IE and PA, induced by the CH_3 (blue) and NO_2 (red) groups, are reported. See the text for further details.

nitro-aromatic derivatives in the case of EAS reactions. In the case of the CH₃ group, a further (weak) electron-attractive inductive effect is expected, due to the fact that the methyl moiety is more electronegative than the H atom, as confirmed by the fact that the *ipso* coefficient only has a positive value. Despite such a weak inductive contribution, the ortho, meta and para coefficients of the CH₃ group are all negative, thus leading to an average IE shift of -0.1 eV estimated in the case of the unsubstituted C atoms of toluene with respect to the benzene value. This negative shift supports the idea that the CH₃ group is able to extend the π -conjugation of benzene through a hyperconjugation mechanism and promotes a better stabilization of core holes. The resonant behavior of CH₃ and NO₂ substituting groups induces opposite effects on the benzene ring, as shown by a comparison between ortho-para and meta coefficients in Table 2. The CH₃ group stabilizes a core hole in ortho-para, in agreement with the stronger negative deviations of the corresponding coefficients; the NO₂ group displays an opposite behavior and destabilize a core hole in ortho-para, in agreement with the stronger positive deviations of the corresponding coefficients. It may be also worth noticing that, coeteris paribus, such positive deviations are more pronounced in the case of C atoms holding ortho positions than in the case of those in para with respect to the NO₂ group. This is in agreement with a quite long range effect of the isotropic contribution of the nitro group to the core holes (blue I^+ labels in Fig. 2), which has to be summed to its R⁺ contribution.

Deeper insight can be provided by performing further analysis beyond the additivity model. In the case of o-nitrotoluene, the twisting of NO2 induced by the ortho-proximity of the methyl group leads to an attenuation of the π -conjugation of the nitro group, which, in turn, seems to suppress its R⁺ effect while not affecting the isotropic inductive contribution. IE values lower than the corresponding additive coefficients have indeed been estimated in the case of the C3 and C5 positions of the o-nitrotoluene (0.41 and 0.39 eV, respectively, in comparison with the expected 0.49 and 0.44 eV values). A direct comparison of the strength of opposite R⁺ and R⁻ effects can be attempted in the case of the *m*-nitrotoluene, where competing effects fall exactly on the same C2, C4 and C6 positions. Quite low IE shifts (0.34, 0.38 and 0.31 eV, respectively, to be compared with the corresponding additive coefficients, 0.39, 0.42 and 0.34 eV) indicate a stronger R⁻ effect of the methyl group; an opposite behavior, if compared with the stronger I⁺ effect of the nitro group, consistent with a predominance of the CH₃ group as a director in EAS reactions.²

3.2 Connection between the methyl group and the aromatic ring: about and beyond the hyperconjugation model

Further calculations have been performed in the framework of the plane wave/pseudopotential method introduced above to shed more light on the connection of the methyl group to the benzene ring, as well as to its relationships with the hyperconjugation mechanism. In detail, we have considered the displacement of the electronic charge density in the toluene molecule and nitrotoluene isomers caused by the formation of a C(1s) core hole. This has been investigated by analysing difference electron density maps, obtained by subtracting the valence electronic density of a ground state calculation from the valence electronic density of the corresponding calculation of a core hole ionized state. The resulting density difference maps, displayed in Fig. 3, show the amounts of charge density flowing from red-colored negative zones to blue-colored positive zones in order to screen the core hole. Three different screening patterns have been identified, which elucidate the relationship between the sp³ methyl carbon and the sp² ring: (i) the R^{-} effect connected to the textbook hyper-conjugative mechanism is fully acknowledged by comparing the screening patterns of a C(1s) core hole induced in the C2 and C3 positions of the p-nitrotoluene (the upper row in Fig. 3). In the case of the C2 position, the CH₃ group (enclosed in a blue ellipse) is more involved in the screening of the core hole, in contrast to the C3 position, where a visibly lesser contribution of the methyl group to the screening is added to the R^+ contribution of the NO₂ group (enclosed in a red ellipse), which is able to drain part of the charge density from the neighboring π -type red zone. (ii) When the core hole is located in the C0 positions (i.e., the methyl carbon, see the middle row in Fig. 3), valence charge is displaced to screen both the almost spherical blue zone around the C0 position and a different π -shaped blue zone centered on the C1 position (see the blue arrows in Fig. 3). The first of these blue zones reflects the expected behavior for a C(1s) core hole, as already pointed out by Bolognesi et al.,6 while the second zone was not observed in the previous study. The π -shaped blue region on the C1 atom indicates that its p_z orbital is involved in the formation of the ionized state and has to be screened by a corresponding amount of valence charge. Apart from the role of the neighboring C1 position, negligible contributions to the screening come from the aromatic ring, indicating that the relationship between the sp³ core hole and the sp² system is not reciprocal with the relationship discussed in (i). (iii) In the case of the C1 maps (the lower row in Fig. 3), the screening pattern of the almost spherical blue zone around the C1 position is dominated by the isotropic I⁺ effect of the neighboring methyl group, not displaying any R⁻ contribution. An expected intraring π -type contribution to the screening of the C1 core hole, comes instead from the C2/C6, and C4 positions (red arrows in Fig. 3), as already discussed elsewhere.6

The above screening patterns provide a guide to the analysis of the corresponding C0 and C1 IE values, even if small differences between IE values do not produce appreciable variations in the charge density maps corresponding to different nitrotoluene isomers. Regarding the calculated IE of C0 positions, all the nitrotoluenes values are quite close to that of toluene (within 0.2 eV, see Fig. 2) indicating that the strong electron-attracting behavior of the nitro group is only slightly propagated to the CH₃ moiety through its connection with the aromatic system. A higher IE value has been calculated for the *p*-nitrotoluene isomer (291.20 eV), where the resonant contribution of the nitro group can affect the displacement of positive charge in the C1 position (Fig. 3). A similar contribution is not expected in the case of *m*-nitrotoluene (291.08 eV), where the C1 atom holds a *meta* position



Fig. 3 Difference density maps (top and side view) of "standard" versus "core-hole" calculations (see the text): (upper row) screening of a core hole induced in the C2 and C3 positions of *p*-nitrotoluene. (Middle row) Screening of a core hole induced in the C0 position of toluene, *o*-nitrotoluene, *m*-nitrotoluene and *p*-nitrotoluene. (Lower row) Screening of a core hole induced in the C1 position of toluene, *m*-nitrotoluene and *p*-nitrotoluene. (Lower row) Screening of a core hole induced in the C1 position of toluene, *o*-nitrotoluene and *p*-nitrotoluene. Blue and red zones represent positive and negative isosurfaces, respectively, of electronic density sampled at 0.002 electrons per a.u.³ (0.005 electrons per a.u.³) in the case of the upper (middle and lower) row: an amount of valence charge density flows from red to blue regions to screen the core hole.

with respect to the nitro group, and in the case of *o*-nitrotoluene (290.82 eV), due to the twisting of the NO₂ group as well as to more complex interference patterns between the two sterically close substituents. All three C1 positions fulfill instead the additivity model, in agreement with the methyl *ipso* coefficient reported in Table 2. They are affected, in contrast to the C0 positions, by the strong NO₂ electronwithdrawing effect; all of the corresponding nitrotoluene IE values are therefore blue-shifted by about 0.5–0.6 eV with respect to that of toluene.

3.3 Correlation between C(1s) ionization energy and proton affinity in nitrotoluene isomers

Protonation enthalpy values calculated at the G3B3 level for the three nitrotoluene isomers are shown in Table 1 and in Fig. 2, where they are also accompanied by the corresponding benzene, toluene and nitrobenzene values calculated by using the same method. As noted above, PA values can be calculated for all the possible protonated intermediates of all the investigated molecules, as opposed to measured values, which are

Paper

available for the most stable intermediates only. The same additive model introduced in Section 3.1 in the case of IE shifts can be applied to PA shifts; data points have been fit with a similar degree of accuracy. The additivity coefficients for protonation of ortho, meta and para positions with respect to the methyl and nitro substituents are reported in Table 2. Protonation enthalpies affected by the position of the NO₂ group are characterized by the expected order (meta < ortho, para), in contrast to the MP2 values mentioned above.41 IE values are now correlated with the present PA values, thus allowing for a close connection between core-ionized and protonated positively charged states involving the same C atom. The present G3B3 investigation has been extended to previous MP2 results related to the mesitylene and to the o-, m-, p-xylene compounds,²³ in order to extend the IE and PA range and, in turn, to achieve a better fitting of data. All of the correlation data are shown in Fig. 4 (a). All data points have been used to obtain the leastsquares fit represented by a red line. Such data points are slightly scattered around this line (correlation coefficient R = 0.9917 and rms = 0.07 eV), as reported in previous contributions,²¹⁻²³ ranging from the strongly activated mesitylene ring, placed at the low-left end of the line, to the strongly deactivated nitrobenzene ring, placed at the high-right end of the line. Positive and negative deviations from the fit line can be analyzed to gain the deepest insight possible into the competing properties of the CH₃ and NO₂ groups in the nitrotoluene isomers as activating and deactivating factors, as well as positional selectivity directors, in EAS reactions.

In this regard, we focus now on the inset (b) of Fig. 4, showing in more detail the nitrotoluenes correlations. First of

all we note that the strong hyper-conjugative effect of the methyl substituent plays a leading role in determining the position of data points scattered (R = 0.7603) both along and across the fit line, that is, in turn, the chemical properties of nitrotoluene compounds. A clear partition between the more activated C2,4,6 atoms, holding ortho and para positions with respect to the CH₃ group, where it can display its R⁻ effect, and the more deactivated C3,5 atoms in meta has been marked by a dashed red line in Fig. 4(b). On the contrary, a substantially meaningless distribution of data points is obtained if we group them according only to their ortho-para or meta position with respect to the NO₂ group. Nevertheless, the NO₂ group acts as a fine modulator of the position of data points. This main achievement can be enriched and supported by further considerations: (i) if we compare the activated C4 and C6 positions of o-nitrotoluene (blue circles) with those of the m- and p-isomers (C2, C4, C6 red circles and C2,6 green circle, respectively), the blue circles correspond to the most activated (i.e. closer to the leftlow end of the distribution) positions of all nitrotoluenes, in agreement with the partial suppression of the conjugation of the NO₂ group to the ring, due to its twisting. (ii) The C4 positions of o- and m-nitrotoluene are the most easily protonated. In the case of the ortho isomer (blue circles), this is in agreement with a stronger R⁻ effect of the CH₃ group on the C4 para than on the C6 ortho position (see Table 2); in the case of the meta isomer (red circles), the large positive shift of the protonation enthalpy in the C6 position is not in agreement with its lowest IE value, compared with those corresponding to the positions C2 and C4. We suggest that the formation of weak H bonds between the methylene H atoms of the σ -complex formed in C2



Fig. 4 (a) Protonation enthalpy of benzene and of different sites of several CH_3 - and NO_2 -substituted benzene rings, plotted against the calculated vertical C(1s) ionization energy of the C protonation site. The red line is the least-squares fit of the calculated data points. Data not reported in Fig. 2 and Table 1 are taken from Myrseth *et al.*²³ (b) Correlation data corresponding to nitrotoluene isomers only are shown in the inset of figure, where the positions of C atoms on the ring are also indicated. A dashed line, orthogonal to the solid line, separates data points corresponding to the C2,4,6 positions from those corresponding to the C3,5 positions.

Table 3 Rates of nitration of nitrotoluenes and distribution of dinitro-products. Measured rate ratios of nitrotoluenes (k_{NT}), with respect to nitrobenzene (k_{NB}), and measured distribution of nitro- and X,Y-dinitro-products related to the competitive nitration of toluene, nitrobenzene and nitrotoluenes in CH₃NO₂ with NO₂PF₆ at 298 K (data taken from Olah, *et al.*^{2,27}). In the cases of nitrotoluene isomers, the C position undergoing nitration is also reported to avoid ambiguity

Species		$k_{\rm NT}/k_{\rm NB}$		Distribution of nitrotoluene products (%)			
Toluene	_			2-NT 68	3-N 2	Г	4-NT 30
Distribution of di-nitrobenzene products (%)							00
Nitrobenzene		1	1,2-Di- 10	NB	1,3-Di-NB 89		1,4-Di-NB 1
		Distribution o	f di-nitrotoluene pr	oducts (%)			
o-Nitrotoluene m-Nitrotoluene p-Nitrotoluene	384 91 147	2,3-Di-NT 1.0 (C3) 42.1 (C2)	2,4-Di-NT 59.0 (C4) — 99.8 (C2)	2,5-Di-NT 0.1 (C5) 18.6 (C6) —	2,6-Di-NT 39.9 (C6) —	3,4-Di-NT — 35.8 (C4) 0.2 (C3)	3,5-Di-NT — 3.5 (C5) —

and C4 and the neighboring NO_2 group, which do not occur in the case of C6, is responsible for the lowering of the C2 and C4 values, which deviate from the distribution expected in terms of the additive model.

We test such an apparently sensitive theoretical machine on a well characterized chemical process such as the nitration by NO₂PF₆ of the toluene, nitrobenzene, and of the three nitrotoluene isomers,^{2,27} whose previously measured parameters are reported in Table 3. Let us consider first the nitration of toluene and nitrobenzene. In both cases the positional selectivity of the reaction is quite low and the expected, close to the statistically determined, distribution of ortho and para products in the case of toluene and meta (with a 10% population of ortho) in the case of nitrobenzene is obtained. The 10% population of ortho-dinitrobenzene obtained in the latter case reflects the lower resonant effect of NO₂, in agreement with the very small difference between the ortho and meta protonation enthalpy values. Concerning the nitrotoluene isomers, let us compare now the measured reaction rates and product distributions reported in Table 3 with the theoretical correlation data shown in Fig. 4(b). If we consider the whole distribution, we note that there is a clear partition in Fig. 4(b) between C positions which are quantitatively nitrated and C positions which are not, the largest separation being between the C2,6 and C3,5 positions of the p-nitrotoluene, in agreement with the most unbalanced distribution of di-nitro products (99.8% vs. 0.2% nitration of such positions). This separation between active and non-active positions have been marked by a dashed line in Fig. 4(b). Active positions are distributed along the fit line in agreement with the $k_{\rm NT}/k_{\rm NB}$ values reported in Table 3, which indicate a faster nitration of o-nitrotoluene, closer to the left-low end of the distribution, with respect to the *meta* and *para* isomers. If we consider each of the nitrotoluene isomers alone, we can correlate the distribution of di-nitro products with the PA of the sites, which is more closely related to the formation energy of the different σ complexes, leading to the final distribution of products. The *p*-nitrotoluene case is straightforward, as mentioned above. In the case of *o*-nitrotoluene, the slight predominance of the 2,4-di-nitro product is in agreement with the higher PA of the C4 position. In the case of *m*-nitrotoluene, the low nitration rate of the C6 position parallels its lowest PA, possibly for the same sterical reason suggested in the previous paragraph. Regarding the C2 and C4 positions, we note that the slight preference for the nitration of the C2 position in a NO₂PF₆/CH₃NO₂ solution is inverted in the case of a similar competitive process in a NO₂PF₆/H₂SO₄ solution,²⁷ thus justifying the apparent disagreement between calculated and measured data.

4 Conclusion

We have performed a joint experimental and theoretical investigation of the three nitrotoluene isomers, aimed at unraveling the complex interplay between the competing effect of the nitroand methyl-substituents on the chemical properties of such a synthetically important class of aromatic compounds. We have pointed out that: (i) accurate ab initio calculations are an essential complement to experimental investigation, in order to achieve the complete assignment of photoemission measurements in the case of congested XPS spectra, as well as to estimate protonation enthalpies in the case of all the eligible sites of the molecule; (ii) textbook models based on inductive and resonant effect of different substituents of the aromatic ring, as well as on the hyper-conjugative connection of the methyl group with the π -conjugated system, can be revisited, at a more quantitative level, by using core-ionization energies of inequivalent atoms as leading quantities; such an analysis can account indeed for minimal oscillations of the core-ionization energies related to the weak, opposite resonant effects of the CH_3 and NO_2 groups. (iii) The analysis of correlation patterns between ab initio calculated proton affinities and core-ionization energies represent a powerful tool, which is able to predict site-specific reactivities of polysubstituted molecules in the case of electrophilic aromatic substitution reactions.

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