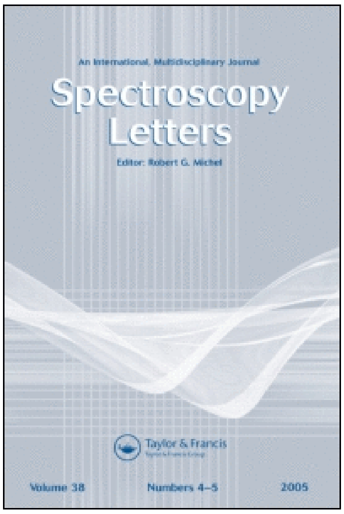

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NEAR UV SPECTRA OF PHENOXYACETIC ACID AND PHENOXYPROPANOIC ACID

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The secondary transition of the benzene molecule lies towards 250-260 nm. It is electronically forbidden because of the D_{6h} symmetry of the molecule. The intensity of the transition is low (ε_{max} = 220 ; medium : cyclohexane) and very sensitive to interactions with the surrounding parts of the molecule likely to perturb the symmetry. Substituents distort all the more the symmetry as their orbitals couple with the orbitals of the π system. [1-6] They increase the intensity of the transition according to a vector scheme taking into account the positions of the substituents around the nucleus, and the strength of their coupling (SKLAR). [7-14] It has been shown that the too much qualitative SKLAR's approach could be superseded by the much more quantitative and more accurate NVM (New Vector Model) [15] grounded on MNDO calculations, or the IVM (Interaction Vector Model) [16-18] using a more empiric approach.

The intensity of the secondary transition is a probe to study the interactions between chromophore and substituents. This allowed to understand the hyperconjugative behaviour of the $-CH_2-$ substituent in $\phi-CH_2-(CH_2)_n-X$ when X is a σ-electron withdrawing group. The $-CH_2-$ group on the chromophore plays the same part as a "bridge", allowing the X group to perturb the π_ϕ system. It changes the σ effects of X into π_ϕ ones. [2-5] Hyperconjugation is a weak interaction, since the secondary transition in toluene is still only : ε_{max} = 265 ; medium : hexane. Substituents such as -OR are much more perturbating, because of the coupling of the pseudo non bonding orbitals of the oxygen atom with the π_ϕ system [phenol : ε_{max} = 2200 (hexane)]. This coupling is π_ϕ electron donating.

In the present paper we should like to study the intensity of the secondary transition in ϕ-OR type molecules, when R is $-CH_2-CO_2H$ (phenoxyacetic acid) or $-(CH_2)_2-CO_2H$ (phenoxypropanoic acid), in connection with the behaviour of the electrons of the oxygen atom. This should lead to understand how these electrons are shared between the substituent and the chromophore, and to understand the incidence of such a behaviour on intensity (see figure 1 for the near UV-spectra). This will allow to test the ability of NVM and IVM to mirror small intensity changes in the series $\phi-O-CH_2CH_3$, $\phi-O-CH_2-CO_2H$, $\phi-O-(CH_2)_2-CO_2H$

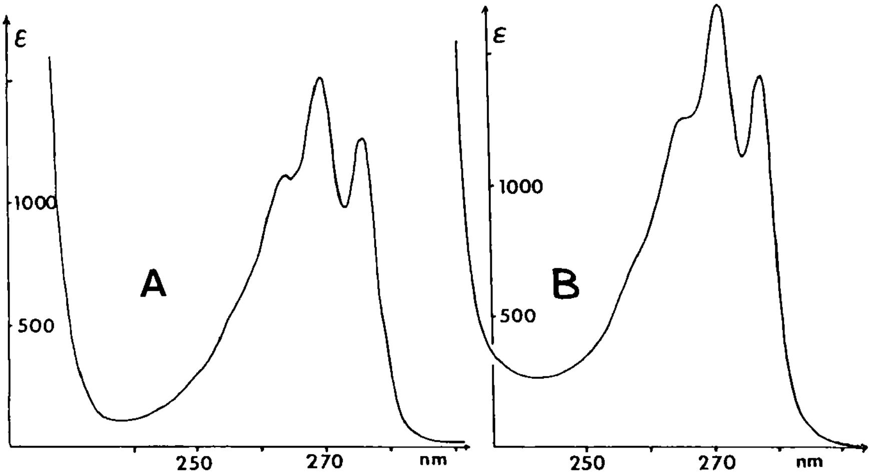

Figure 1. A) Near UV spectrum of phenoxyacetic acid ϕ-O-CH_2-CO_2H. ε_{max} = 1510, λ_{max} = 269 nm (medium : methanol) ; ε_{sm} = 1260.
B) Near UV spectrum of phenoxy-3-propanoic acid. ϕ-O-CH_2-CH_2-CO_2H. ε_{max} = 1685, λ_{max} = 270 nm (medium : methanol) ; ε_{sm} = 1410.

when substituents impose similar electronic effects upon the chromophore. Furthermore, the two acids above, particularly the phenoxyacetic acid molecule, are parent compounds of herbicids series, and their study is of interest for our laboratory whose focus is on plant chemistry.

I - THE NEW VECTOR MODEL (NVM) AND THE PHENOXYACETIC AND PHENOXYPROPANOIC ACIDS SPECTRA

The NVM approach is based on MNDO calculations. It leads to a simple relationship, already used to study π-donating substituents such as -CH_3, -OH, -OCH_3 :

$$\varepsilon_{sm} = 4905\ (TS + V)$$

ε_{sm} is the maximum of the smoothed absorption curve (BALLESTER and RIERA [19]). ε_{sm} minimizes the incidence of the vibrational fine structure on the measure of intensity. The above relationship has been used mainly for molecules with weak steric strain (no fused rings). It has been extended to molecules with fused rings, taking into account the strain effect as a strain vector assumed to be a component of the transition moment vector. [15]

V is a vibrationnal component to the intensity :

$$V = 0.0180 + 0.0390\ K + 0.0030\ (n_C + n_O)\quad ;\ \text{if } n_O = 0 : K = 0\ ;\ \text{if } n_O \neq 0 : K = 1$$

n_C is the number of alkyl substituents, n_O the number of alkoxy ones.

T is grounded on the combination of the moduli (t_1 and t_2) of two vectors : $\mathbf{t}_1$ and $\mathbf{t}_2$.

$\mathbf{t}_1$ is the transition moment vector as defined by the SKLAR's simple vector model. [15-17] The moduli of the six component vectors related to the six positions around the chromophore are used to calculate $\mathbf{t}_1$. They are given a MNDO basis : the modulus of the component vector of a given position on the chromophore is the π bond order of the bond C_ϕ-X, X being the substituent. $\mathbf{t}_1$ strongly takes into account the whole part of the π system outside of the benzene moiety.

t_2 is the modulus of the vector $\mathbf{t}_2$ calculated when using only the two π highest occupied molecular orbitals of the ground state (corresponding to the degenerate HOMO in the free benzene molecule), since these orbitals are the most important as far as the ground state is concerned in the transition. The evaluation of the modulus of the component vector on a given carbon atom of the ring is calculated from the distorsion of the π density (only the part of the π density related to these two orbitals) from what is observed in the benzene molecule itself. Thus, t_2 puts the emphasis on the electrons of the benzene moiety which have the highest energies. t, is a combination of t_1 and t_2 :

$$t = [t_2 + (0.3214/t_2)t_1] / [1 + 0.3214/t_2] \Rightarrow T = t\,\delta$$

$$\text{with : } \delta = 1/(1+\Delta)^{0.5} \text{ and } \Delta = 2|t_1 - t_2| / (t_1 + t_2)$$

The vectors $\mathbf{t}_1$ and $\mathbf{t}_2$ should be colinear, since each one of them represents the transition moment. In fact, they would be perfectly equal if the two approaches were perfectly equivalent. The angle between them is always low. To be simple, one uses a combination of their moduli. T is the modulus of a vector **T**.

S is another approach to the transition moment. It is related to a sort of photonic cross section. It emphasizes the act of capturing photons. Actually, its value increases as much as the substituents coupled to the π system enlarge the π system, increasing its efficiency to capture photons. S is given by the relationship :

$$S = [5n_O/(4{,}8 + 0.2\,n_O^2)] + n_C/(4{,}8 + 0.2\,n_C^{(2+0.5\,n_O)})$$

n_C is the number of alkyl substituents, n_O the number of -OR ones. In the present work there is no alkyl substituent : $n_C = 0$. Thus, one should use the value obtained for ϕ-OR when $n_O = 1$, that is to say : S = 1. In fact, R in the substituent is not purely aliphatic, since there is an electron-withdrawing group on the aliphatic chain. The above relationship, which is designed to take into account the effects of several substituents around the benzene nucleus, can be fitted to the present case, when there is a single substituent, to reach a better accuracy. It has been shown in a preceding work (when a π donating substituent is involved, near to an alkyl or to a methoxy group) that the next relationship can be used to approach S for a monosubstituted molecule : [18]

$$S = 5.2812(D\cdot P^{1.43})^{(1/2.43)}$$

D is the increase of the number of π electrons caused by the substituent. *P* is the π bond order between the phenoxy oxygen atom and the carbon to which this atom is bonded in the benzene chromophore (C_ϕ-O).

The standard NVM relationship has been given here above to calculate V. Nevertheless, the R part of the substituent differs slightly from a pure aliphatic one. The next relationship has been established for monosubstituted molecules displaying substituents similar to akyl or alkoxy groups :[18]

$$V = 0.03375\,S^2 + 0.00825\,S + 0.01800$$

For phenoxyacetic acid : V = 0.0533. For a pure -OR substituent it would be : 0.0600. In the present work this correction is of little effect since V is only a very small part of intensity.

Four conformations of phenoxyacetic acid have been studied (ϕ-O-C being considered as planar since this is the case for phenol and anisole which display very similar spectra) : a plane one (PA1, Figure 2), apart from the two hydrogen atoms of the $-CH_2-$ group which lie above and below the plane of the molecule. Another conformation (PA2), when the dihedral angle between the $-CO_2H$ plane and the ϕ-O-C plane is first assumed 90° (ϕ-O-C-C lie in the same plane), and then optimized (result : 104°, which lengthens the distance between -O- of the ϕ-O group, and C=O). The third conformation (PA3) is obtained when starting from a 90° dihedral angle between the four atoms C_{ϕ}-O-C_{H2}-C_{O2H}, the C=O bond eclipsing the C_{H2}-O bond. The optimization of the geometry of the whole molecule leads to conserve the eclipse and the orthogonal dihedral angle (this angle is increased less than 2°). For PA4 the starting conformation is the same as PA3, except for the C=O bond which is rotated 90° from its eclipsing position. When optimization of the whole geometry is reached this angle is 94°, and the dihedral orthogonal angle is conserved. All these conformations display similar energies. Nevertheless, PA2 displays the lowest one. Taking this one as a reference, the other display the next values : + 0.040 eV (PA1), + 0.038 eV (PA3), + 0.042 eV (PA4). The average conformation should be nearer to PA2. Furthermore, although the atom of the substituents lie in very different positions, next calculations show that these four conformations should display almost the same behaviour as concerns intensity. This shows that the effects of the substituent on the π system are mainly transfered through the chain than directly through space.

Intensity calculations are given for phenetole (ϕ-O-CH_2-CH_3) as a reference to evaluate the effects of the $-CO_2H$ group on the benzene nucleus. The conformation used is the plane one. The carbons of the chain lie in the plane of the ϕ-O part, the dihedral angle ϕ-O-C-C being 180°, with a staggered conformation for the ethyl part. This plane conformation is more stable than the conformation when the dihedral angle ϕ-O-C-C is assumed 90°. The whole geometry is optimized. Nevertheless, this calculation does not take into account the high possibilities of free rotation within the substituent. Phenetole will be named when necessary : PHE.

d_{π} is the number of π_{ϕ} electrons. *D* is the increase of the number of π_{ϕ} electrons caused by the substituent. MNDO calculations lead to the values in table I .

The difference with experiment is only - 4.3% as concerns PA1, and - 5.6% as concerns PA2, - 7.9% as concerns PA3. A difference lower than ± 10% has been considered as satisfactory in previous calculations. PA4 which is the less favoured conformation displays the worst fitting with

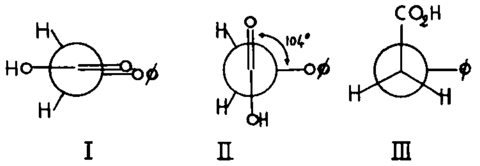

Figure 2. I) conformation PA1. II) Conformation PA2. III) Conformation PA3. The C=O bond eclipses the C-O_{ϕ} one. As concerns PA4 the dihedral angle O=C-C-O is 94°. In the whole conformations φ-O-C are in a same plane perpendicular to the plane of the figure.

TABLE I

[phenoxyacetic acid (PA), and phenetole (PHE). New Vector Model]

	d_{π}	D	P	t_1	t_2	t	S	V	$\varepsilon_{sm,c}$
PA1	6.0818	0.0818	0.2888	0.2888	0.1899	0.2521	0.9076	0.0533	1205
PA2	6.0810	0.0810	0.2874	0.2874	0.1877	0.2506	0.9014	0.0529	1190
PA3	6.0788	0.0788	0.2843	0.2843	0.1862	0.2483	0.8857	0.0518	1160
PA4	6.0771	0.0771	0.2796	0.2796	0.1835	0.2282	0.8689	0.0506	1065
PHE	6.0892	0.0892	0.3029	0.3029	0.2136	0.2672	0.9672	0.0575	1375

Experiment : ε_{sm} = **1260** for the phenoxyacetic acid, and **1515** for phenetole (medium : methanol).

experiment (- 15.4%). PA2 is the most representative conformation and calculations are in good agreement with experiment (- 5.6%). For phenetole, calculation is - 9.2% lower than experiment.

Only two conformations of phenoxypropanoic acid have been studied because of the possible free rotation inside the chain of the substituent. φ-O-C-C-C are in a same plane with a 180° dihedral O-C-C-C angle. PP1 is the plane conformation to be compared to PA1, and PP2 is to be compared to PA2 which is the lowest energy one of the four conformations of phenoxyacetic acid studied. PP2, too, is 0.06 eV lower than PP1. Calculated intensities are higher than those obtained for PA.

Again conformation does not play a major part in the intensity. The results for PP1 and PP2 respectively are - 8.3 %, and - 9.6 % lower than experiment. This is near to 10%, but still lower.

I - THE BASIS OF THE IVM

Within the IVM [16,17] as in the NVM, the SKLAR's simple vector scheme approach is used with basis vectors **n** whose moduli n depend on the nature of the substituents. These moduli are grounded on the

TABLE II
(phenoxypropanoic acid. New Vector Model)

	d_π	D	P	t_1	t_2	t	S	V	$\varepsilon_{sm,c}$
PP1	6.0859	0.0859	0.2966	0.2966	0.2016	0.2600	0.9408	0.0556	1294
PP2	6.0850	0.0850	0.2949	0.2949	0.1995	0.2584	0.9332	0.0551	1275

Experiment : ε_{sm} = **1410** for the phenoxypropanoic acid (medium : methanol).

experimental spectroscopic data of the monosubstitued chromophore. Thus, a n value is no more a MNDO calculated one using the HOMOs. Another concept of major importance has been introduced compared to the NVM one, and it completely changes the nature of the approach : the *interaction vector*. The modulus of this vector involving two substituents, is calculated on spectroscopic data of ortho, meta and para disubstituted chromophores. Its direction bisects the angle between the two interacting basis vectors. Interaction vectors are of no use here since the chromophore is monosubstituted. S is used as in the NVM. In fact, it is used as $\sigma = S^{1/2}$. As S and V have been calculated here above on a finer basis using MNDO, one shall use the above calculated values. n is obtained using the next relationship : [18]

$$n = -0.5204 + (0.27082 + 0.55801\ S)^{0.5}$$

It takes into account the fact that the substituent is not a pure -OR group. This relationship leads to : n = 0.3612 for PA1, when it is 0.3900 for a pure -OR group.

Within the IVM one defines a, b, p, k, d. a is : $a = n^{1.5}\sigma^{0.5}$, and b : $b = n(n + \sigma)/2$. Then : $p = (a + kb)/(1 + k)$, with $k = d^6$, and : $d = |n - \sigma|$. Thus : $\varepsilon_{sm,c} = 4905\ [1.025\ p + V]$.

As concerns PA1 : $\sigma = 0.9527$, $n = 0.3612$, $a = 0.2119$, $b = 0.2373$, $d^6 = 0.0428$, $p = 0.2129$, thus $\varepsilon_{sm,c} = 4905\ (1.025 \cdot 0.2129 + 0.0533) = 1330$. This calculated value is + 5.7% higher than experiment, which is satisfactory.

As concerns PA2, $\sigma = 0.9494$, $n = 0.3593$, $a = 0.2100$, $b = 0.2351$, $d^6 = 0.0422$, $p = 0.2110$, $V = 0.0529$. Thus : $\varepsilon_{sm,c} = 4905(1.025 \cdot 0.2110 + 0.0529) = 1320$, which is only + 4.8% higher than experiment.

PA3 leads to : $\sigma = 0.9411$, $n = 0.3543$, $a = 0.2046$, $b = 0.2295$, $d^6 = 0.0408$, $p = 0.2056$, $V = 0.0518$. $\varepsilon_{sm,c} = 1288$. This is + 2,2% higher than experiment.

PA4 leads to : $\sigma = 0.9321$, $n = 0.3489$, $a = 0.1990$, $b = 0.2235$, $d^6 = 0.0393$ $p = 0.1999$, $V = 0.0506$. Thus : $\varepsilon_{sm,c} = 1253$.

NVM is nearer to experiment than IVM. In fact this does not mean that NVM is better. Both of the methods are within the ± 10% range which is considered as satisfactory. PA2 being the favoured conformation, the values obtained for that conformation are representative of the methods : 1190 for NVM and 1320 for IVM.

As concerns the phenoxypropanoic acid PP1 : σ = 0.9699, n = 0.3717, a = 0.2231, b = 0.2493, d^6 = 0.0458, p = 0.2243, V = 0.0556. Thus : $\varepsilon_{sm,c}$ = 1400, which is only - 0.01% lower than experiment.

PP2 : σ = 0.9661, n = 0.3693, a = 0.2206, b = 0.2466, d^6 = 0.0452, p = 0.2217 V = 0.0551. Thus : $\varepsilon_{sm,c}$ = 1385, which is only - 0.02% lower than experiment.

As concerns phenetole (PHE) : σ = 0.9834, n = 0.3799, a = 0.2322, b = 0.2590, d^6 = 0.0483, p = 0.2334, V = 0.0575. Thus : $\varepsilon_{sm,c}$ = 1455, which is only - 4.5% lower than experiment.

The better results obtained using the IVM enlighten the efficiency of the parametrization approach used in that model. Intensity for the monosubstituted chromophore can be reached on the only ground of three factors : *P*, the π bond order between the oxygen and the carbon of the ring to which the oxygen is linked, *D* the number of π electrons given to the ring, and S and V which depend in fact on the preceding factors.

II - COMMENTS ON THE ORIGIN OF THE INTENSITIES

Phenol, anisole and phenetole

As far as spectroscopy is concerned, phenol, anisole and phenetole are the parent compounds of phenoxyacetic acid and phenoxypropanoic acid.

The plane conformation of phenetole has been used in these calculations. As concerns the geometry used for anisole, one of the hydrogen atoms of the methyl group lies in the plane of the benzene moiety. Other geometry data of the whole molecules have been optimized.

The number of π electrons in the $p_{z,O}$ non bonding orbital of the oxygen atom, that is to say the p_π orbital of the oxygen atom, which is coupled to the π_ϕ system, is 1.8820 in phenetole, and 1.8813 in anisole. This is lower than what is observed in phenol : 1.9068. This decrease is surprising since an alkyl group is π and σ electron donating. The π donating character arises from hyperconjugation. Hyperconjugation is related to the ability of the methylene $-CH_2-$ of the ethyl group, or to the ability of the methyl group, to couple an antisymetric combinations of the hydrogen *1s* orbitals to the π symetry orbitals belonging to π groups, or to p_π orbitals of other atoms. This is the case here with the $p_{z,O}$ non bonding atomic orbital of the oxygen atom which separates the alkyl group from the benzene moiety. The number of π_ϕ electrons is : 6.0932 in phenol, and lower : 6.0893 electrons in anisole, and 6.0892, in phenetole [unless particular caution should be taken in calculations, as concerns possible conformations, it is difficult to distinguish the π_ϕ behaviour of anisole and phenetole]. Thus, contrary to what could be attended : changing the H of OH by an alkyl group, which is known to be π and σ donating, decreases the number of π_ϕ electrons as well as the number of $p_{z,O}$ ones.

In fact, in phenol the charge of the ϕ-O moiety is - 0.1929 ; the charge of the hydrogen of -OH is of course + 0.1929. In anisole the charge of the ϕ-O moiety is - 0.2014, and that of the methyl group is + 0.2014. This is the proof that the methyl is electron donating to the ϕ-O moiety. The number of π_ϕ electrons and $p_{z,O}$ electrons decreasing, means that the methyl, or the alkyl group, increases the number of electrons in the σ frame of the the ϕ-o moiety.

In the phenol molecule the oxygen atom displays a charge of - 0.2474 although it looses 0.0932 π electron from its $p_{z,O}$ orbital. That means that it withdraws 0.2474 + 0.0932 = 0.3406 electron from the σ system. Actually, oxygen is known to be a stronger σ withdrawing center than a π donating one.

The problem is slightly more complex in phenetole and anisole owing to the alkyl group which displays a π and a σ behaviour. In order to understand, it is necessary to separate these two effects at the level of the methylene group linked to the oxygen atom, since the OA of that group are involved in an hyperconjugative coupling with de $p_{z,O}$ orbital of the oxygen atom, and further with the π_{ϕ} system of the benzene moiety. For doing this, which has never been done, we separate the π symmetry molecular orbitals from the others, and in these OM one adds the electron densities which are in the 1*s* OA of the hydrogen of -CH_2-. The same is done for the σ-symmetry molecular orbitals (the others).

In anisole, the electron density on an hydrogen involved in the hyperconjugative coupling (there are two hydrogens involved, the third one is assumed lying in the plane of the ring) is 1.015 electron. 0.565 electron is in the π symmetry system, and 0.450 electron in the σ one. One will say that the electrons of these hydrogens belong for 55.7% to the π system and for 44.3% to the σ one. It is quite astonishing that for such a conformation the electrons in the OA of the hydrogen atoms displays more π than σ character. This has never been underlined. In order to compare this result to a more standard hyperconjugation scheme, the same calculation has been done for the methyl group of the toluene molecule, in a similar conformation : one of the hydrogen atoms lies in the plane of the benzene ring. The electrons of the hydrogen atoms involved in the hyperconjugative process display 53.8% π character. This result confirms the above one. Nevertheless, it could lead to think that the methyl group, as concerns toluene, is less involved in the σ,π hyperconjugative coupling than it is in anisole, although hyperconjugation has been related to a σ interaction with π systems, the toluene molecule being a sort of archetype of hyperconjugation. In the anisole molecule, the "hyperconjugation" pattern involves a $p_{z,O}$ "non bonding" orbital, and not a classic π system. Furthermore, playing the part of a σ,π bridge the hyperconjugation of the -CH_2- group in anisole allows the π type electrons to be attracted by the σ electron withdrawing power of the oxygen atom, and a fraction of these electrons is found in the σ part of the molecule. This will be studied underneath.

In anisole, the electron density of the hydrogen atom lying in the plane, is 0.9836 σ electron. Considering as a whole the three hydrogen atoms of the methyle, the π identity of their electrons is 37.5 %. This is lower than above but still quite a striking and unexpected result. Confirmation arises from toluene, whose result is still lower : 35.8%.

In phenetole the π identity of the electrons of the methylene hydrogen atoms is 55.5 %, and their σ identity 44.5%. The electrons of the hydrogens belonging to the methylene of the methyl group display a 54 % π character and a 46 % σ one. These results concerning toluene, anisole and phenetole, underline the strong importance of the alkyl group in the electron tranfer between the π and the σ system. The importance is unexpected in anisole and phenetole.

Such a contribution of the alkyl groups to the π systems of anisole and phenetole, forbids to compare these groups to the hydrogen atom of -OH in phenol. This latter atom belongs only to the σ system. Although they bear almost the same charges : + 0.1929 for H in phenol, + 0.2014 for the whole $-CH_3$ in anisole and + 0.1973 for the whole $-C_2H_5$ in phenetole, they do not display the same part in the electron exchange. Actually, the π hyperconjugative coupling of the alkyl group with the oxygen atom and further with the benzene moiety explains the decrease of the number of the π type electrons in these two centers, compared to the phenol molecule. Hyperconjugation mixing π and σ systems allows the $\pi_{\phi\text{-O}}$ electrons to go into the σ frame since, so doing, they lower their energies reaching a more stable state. The oxygen atom plays a central part in the exchange. It looses π electrons from its $p_{z,O}$ orbital, but a part of the electrons that it looses, compared to phenol, goes in the σ part of the oxygen atom because the oxygen atom is a σ electron attracting center (strongly electronegative). In phenol (or when faced to other π systems), the oxygen $p_{z,O}$ orbital gives electrons to the π_ϕ system only because $p_{z,O}$ is a saturated orbital (two electrons). The fact that there is a gift is irrespective of the relative potentials of the $p_{z,O}$ orbital and of the π_ϕ system. Actually, a low energy electron rich orbital p_l (for exemple having two electrons) can give electrons to a higher energy one p_h if that higher orbital is electron poor (for example no electron at all), and if the two orbitals display the right symmetry to couple. The coupling imposes a low lying combination : $\psi = l\ p_l + h\ p_h$ and a high one $\psi = h\ p_l - l\ p_h$. with $l > h$ and $l^2 + h^2 = 1$. The low lying combination is the most populated, (in anisole and phenetole $p_{z,O}$ involves two electrons), with $2l^2$ electron in p_l and $2h^2$ in p_h. The poorer orbital acquires electrons although, before establishing the coupling, it is higher in energy. Thus, the σ charge of the oxygen atom in phenol is - 0.3406, it increases to - 0.4036 in anisole and - 0.3994 in phenetole because of the hyperconjugative σ,π coupling which allows the σ core of the oxygen to withdraw electrons from the π type system.

The $-CH_3$ group when directly bonded to a π system gives some of its electrons to that system. When the $-CH_3$ group is bonded to an oxygen atom, as in anisole, it prevents the oxygen atom to give its π type electrons to the higher energy π_ϕ system to which that latter atom is bonded. Actually, the methyl group bridges the π and the σ system, and so doing it allows the oxygen atom to withdraw a part of the higher energy π_ϕ electrons and a part of its own higher energy $p_{z,O}$ electrons towards its σ core — because oxygen is a strong electron withdrawing center — .

The above results could lead to think that intensity should decrease when going from phenol to anisole and phenetole : the number of π_ϕ electrons decreases [which decreases the probability for a photon to reach an electron] ; the distorsion of the HOMO densities from a pure benzene distribution decreases, which restaures the benzene symmetry and enhances the forbidden character of the secondary transition ; the π bond order between O and ϕ decreases too, etc.

On the contrary intensity increases (phenol : $\varepsilon_{sm} = 1450$; anisole : 1500 ; phenetole : 1515). In fact, things are far from being so desperate as they look. The difference between phenol and phenetole is only 4.4%. UV experiments allow a ± 5% accuracy for ε and ε_{sm}. Furthermore, NVM and IVM calculations have been previously considered as fitting with experiment within a ± 10% margin. One should remind too that NVM and IVM have been parametrized so as to give the same value for the $\varepsilon_{sm,c}$ of phenol and anisole, although experiment for the first one is 1450 and 1500 for the other. Another important point is the incidence of possible conformations on intensity. It has not been taken into account. IVM and NVM agree well with experiment within the error margin, but the experiment differences are weaker than that margin. Phenol, anisole and phenetole are too much similar to allow to explain their intensity differences. The above approach should be more successfull when comparing much more different molecules, as it is attempted underneath.

Phenoxyacetic acid

Owing to the conformation of the $-CH_2-CO_2H$ group, the two hydrogen atoms of the methylene group are not equivalent. Nevertheless, the average contribution of their electrons to the π system is 51.5% and the contribution to the σ one : 48.5%. The percentage of π contribution decreases compared to anisole and phenetole.

The hydrogen atoms of the methylene group involved in hyperconjugation display a negative charge in anisole (- 0.0150 for one hydrogen), still a negative one in phenetole (- 0.0061) but much lower, and a positive one in phenoxyacetic acid (average : + 0.0223). The net charge of the whole $-CH_2-$ is + 0.1850 in anisole, + 0.1591 in phenetole, and + 0.02604 in phenoxyacetic acid. This is consistent with the withdrawing character of the $-CO_2H$ group.

Paradoxically, although it decreases the electron density on the methylene group, the $-CO_2H$ electron withdrawing group does not decrease the electron density in the $p_{z,O}$ orbital : 1.8890, when it is 1.8816 in anisole, and 1.8820 in phenetole (1.9068 in phenol). There is a small increase when a strong decrease is expected. This could be linked to the fact that the π identity of the electrons of the methylene decreases, and then the "bridge" between the electron withdrawing group and the electrons of the $p_{z,O}$ orbital is less efficient. Nevertheless, the number of π electrons is 6.0810 in phenoxyacetic acid, when it is 6.0893 in anisole, 6.0892 in phenetole (and 6.0932 in phenol). This is consistent with the withdrawing character of the $-CO_2H$ group. Thus, $p_{z,O}$ and π_ϕ being part of the same π system, why does the number of electrons in $p_{z,O}$ increase (or at least does not change), and why does that number decrease in π_ϕ ?

In anisole, for example, the π charge on the oxygen atom (ie: the charge in the $p_{z,O}$ orbital) is : + 0.1184, and the σ one : - 0.4036 ; the net charge is : - 0.2853. As concerns the phenoxyacetic acid the π charge is : + 0.1110, the σ one : - 0.3877, the net charge : - 0.2767. The net (negative) charge decreases because of the electron attracting effect of $-CO_2H$. Thus, although the number of π type electrons is increased, or almost kept constant, on the oxygen atom, the number of σ ones is decreased. The electron withdrawing effect of $-CO_2H$ is mainly a σ effect in the conformation studied. This allows to give the answer to the above question concerning the increase of the number of $p_{z,O}$ electrons. Explanation lies in the fact that the decrease of the number of electrons in the σ core causes the σ core to be less negative, decreasing the repulsion with the $p_{z,O}$ π electrons, and doing so an increase of the number of these latter electrons is allowed. Thus, the slight increase of the number of $p_{z,O}$ π electrons, when the number of π_ϕ electrons decreases, does not mean that -CO_2H withdraws the π_ϕ electrons by an other way than through an extended hyperconjugative effect (which involves -CH_2- and $p_{z,O}$). The $p_{z,O}$ orbital and the -CH_2- system still play the part of a bridge between the σ effect of the -CO_2H and the π_ϕ system. More electrons stay in the $p_{z,O}$ orbital, and that does not mean that $p_{z,O}$ could be less involved in the transfer. Actually, for symmetry reasons -CO_2H needs a π coupling with the π_ϕ system to withdraw the electrons belonging to that system, and the only possible π coupling is through $p_{z,O}$ and -CH_2-. The surprise lies only in the fact — here above explained — that the coupling allows an increase of the $p_{z,O}$ electrons.

Thus -CO_2H being able to withdraw π_ϕ electrons through the hyperconjugative σ,π coupling involving -CH_2- and $p_{z,O}$, although the number of $p_{z,O}$ electrons increases, the intensity of the secondary transition should decrease when going from the ϕ-OR type molecules to the phenoxyacetic acid one. Actually, it decreases from ε_{sm} = 1450-1515 to 1260. The two models [NVM (1375 ; phenetole) ⇒ (1190 ; phenoxyacetic acid) and IVM (1455 ; phenetole) ⇒ (1320 ; phenoxyaxetic acid)], mirror correctly the phenomenon. The decrease of the number of π_ϕ electrons decreases the probability for a photon to reach an electron (thus S decreases) ; the distorsion from a pure benzene distribution of the HOMO densities decreases, which restaures the benzene symmetry and enhances the forbidden character of the secondary transition. The methylene is the cause of the decrease of the intensity of the secondary transition although an alkyl group is supposed to be a π donating group, because it allows, through the σ,π coupling in the -CH_2- group, the lower energy σ system of -CO_2H to withdraw electrons from the π_ϕ one.

Phenoxyproanoic acid

The influence of the electron withdrawing -CO_2H group on π_ϕ should decrease compared to phenoxyacetic acid, since that group is farther from the ϕ-O moiety, and the whole calculations and data should lie between those obtained for phenetole and penoxyacetic acid.

The hydrogen atom of -CH_2- on the same side of the plane of the benzene chromophore as C=O displays 54.3 % of π character for its electrons. It is 53.2 % for the other hydrogen atom. It is 55.5 in phenetole and 51.5 in phenoxyacetic acid. d_π, D, and P, display the right order (tables I and II). As concerns intensities the same happens. Experiment gives : ε_{sm} = 1260, 1410, 1515, respectively for : phenoxyacetic acid, phenoxypropanoic acid, and phenetole. The NVM calculations lead to : 1190, 1275, 1375, and the IVM ones to : 1320, 1385, 1455. Intensities increase when lengthening the chain and thus decreasing the -CO_2H effect.

CONCLUSION

The behaviour of phenoxyacetic acid and phenoxypropanoic acid confirms the ability of the NVM and IVM to fit with experiment. The intensity of the secondary transition of the benzene chromophore depends on the efficiency of the hyperconjugative bridge assumed by the -CH_2- group between the chain and the $p_{z,O}$ orbital. This bridge allows the -CO_2H to impose its electron withdrawing effects on the π_ϕ

chromophore. It is in fact an extended hyperconjugative effect since $-CH_2-$ couples with the $p_{z,O}$ orbital, and it is through such a coupling that the effect of the chain can be imposed upon the chromophore.

The extended hyperconjugative effect shows that it is possible that the $-CO_2H$ group withdraws π_ϕ electrons from the chromophore, although it increases the number of π type electrons on the oxygen atom (in the $p_{z,O}$ orbital) which is between ϕ and $-CO_2H$, and nearer to that latter group. This phenomenon arises from the fact that $-CO_2H$ being a strong σ withdrawing group decreases the number of σ electrons on the oxygen atom, and so doing decreases the interelectronic energy with the electrons in the $p_{z,O}$ orbital.

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