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Protonation and Proton Affinity of Anisole. A Theoretical Study

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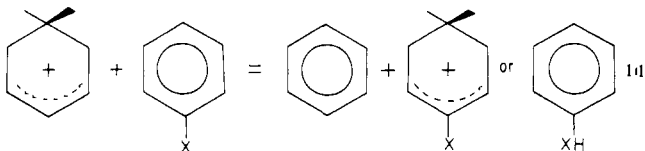
Contribution from the Departamento de Química Física y Química Cuántica, Centro Coordinado SCIC-UAM, Universidad Autónoma de Madrid, Cantoblanco, Madrid-34, Spain. Received July 18, 1978

Abstract: We have performed an ab initio study of the protonation of anisole. From linear correlations between experimental proton affinities and theoretical $1s$ binding energies of para carbon and oxygen atoms we conclude that anisole is a stronger base than phenol, in agreement with experimental evidence. Theoretically predicted protonation sites depend on the conformation of the methoxy group relative to the aromatic ring.

I. Introduction

Considerable effort has been devoted to studying the basicity of aromatic compounds and the intrinsic substituent effects on this property.¹ This has been possible because, at present, gas-phase proton affinities can be measured with high accuracy, using different techniques.² Measured values are not affected by solvent effects and therefore they can be directly compared with those obtained from theoretical calculations, most of which evaluate the energy change in the "isodesmic" proton transfer reaction.³

In general, good agreement was attained⁴ between these theoretical values and the experimental enthalpy change for reaction 1, although there are some exceptions. The experi-



mental proton affinity for anisole is 4.40 kcal/mol higher than that of phenol.⁵ The theoretical energy change⁵ for the "isodesmic" reaction for phenol is a little greater (16.0 kcal/mol) than that of anisole (15.7 kcal/mol). The reason of this disagreement is not clear.⁵ Moreover, it is not well established if these systems protonate on the substituent or on the ring.⁵⁻⁸

We present in this paper ab initio calculations on anisole and phenol to show that the particular conformation of the methoxy group relative to the aromatic ring has a strong influence on the protonation of anisole.

II. Results and Discussion

We have recently proved⁹ that there is a good linear correlation between experimental proton affinities and theoretical

$1s$ binding energy of the para carbon atom for those mono-substituted benzenes that protonate on the ring. The relationship

$$PA = 1035.75E_{C_{1s}} + 11\,607.97$$

$$r = 0.977, \sigma_{PA} = 1.0 \text{ kcal/mol} \quad (2)$$

where the experimental proton affinity (PA) is in kcal/mol and the C_{1s} orbital energy ($E_{C_{1s}}$) is in atomic units, is similar to that proposed by Benoit and Harrison¹⁰ between O_{1s} binding energies and proton affinity values of oxygen bases. We have also shown that eq 2 is applicable to all positions of the ring.¹¹

We have carried out an ab initio calculation of anisole, using a STO-3G minimal basis set¹² and the experimental geometry of ref 13. Using eq 2 we have obtained the ring proton affinities that are presented in Figure 1. The PA value for protonation on the oxygen was obtained from the relationship

$$PA = 311.00E_{O_{1s}} + 6506.44$$

$$r = 0.999, \sigma_{PA} = 0.85 \text{ kcal/mol} \quad (3)$$

where PA is in kcal/mol and $E_{O_{1s}}$ in atomic units.

This equation was obtained from O_{1s} binding energies and experimental proton affinities for benzaldehyde,⁵ acetophenone,¹ and phenolate, 3-hydroxyphenolate, and 3-fluorophenolate anions.¹⁴

The values obtained for σ_{PA} in eq 2 and 3 are smaller than those found by Benoit and Harrison¹⁰ for the linear correlation between experimental O_{1s} binding energies and proton affinities for carbonyl and single-bonded oxygen compounds. However, more recent experimental proton affinity values result in a considerable decrease of their σ_{PA} . The value reported by Benoit and Harrison for single-bonded oxygen

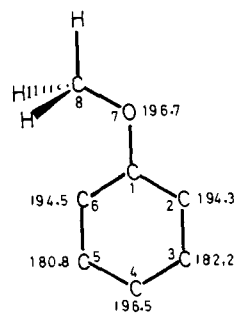


Figure 1. Proton affinities calculated using eq 2 and 3 for anisole in the planar conformation. All values are in kcal/mol.

compounds is $\sigma_{PA} = 0.07$ eV (1.61 kcal/mol); using the experimental ionization potentials given by these authors and the experimental proton affinities of ref 15 the new value of σ_{PA} is 0.04 eV (0.92 kcal/mol).

For the 13 carbonyl compounds that are studied in both ref 10 and 15, using the PA values of ref 10, σ_{PA} is 0.12 eV (2.77 kcal/mol), while the PA values of ref 15 give a σ_{PA} equal to 0.05 eV (1.15 kcal/mol). Moreover, when the more precise experimental core ionization potentials, recently published by Smith and Thomas,¹⁶ are used for (seven of) these carbonyl compounds, the σ_{PA} of the corresponding correlation is even lower (0.023 eV, 0.53 kcal/mol).

According to our results (see Figure 1), the predicted value of the ring PA for anisole is bigger than the one for phenol,⁹ although the difference (2.5 kcal/mol) is still smaller than the experimental value. On the other hand, we found an oxygen PA of the same order as the ring PA.

In a recent paper, Seip and Seip¹³ found that at 523 K the methoxy group of anisole is not in the molecular plane, but it is twisted so that the dihedral angle $C_2C_1O_7C_8$ (see Figure 1) is about 40° . However, the problem of the conformation of the methoxy group relative to the ring, in this compound, is not solved in a conclusive way, either from a theoretical or an experimental point of view.

Theoretical calculations carried out by Hehre et al.¹⁷ using a STO-3G minimal basis set and the standard geometry model of Pople and Gordon¹⁸ found the orthogonal form as the most stable one. However, this result must be taken with caution, since the same authors postulate that a full geometry optimization would probably result in a more stable planar form. Unfortunately, such a calculation is prohibitive and the question is still open.

This is not the case with a very similar compound: phenol. It is well established that phenol is a planar molecule, with a rotational barrier of the order of 3.3 kcal/mol (3.28 and 3.36 kcal/mol by microwave spectroscopy^{19,20} and 3.47 and 3.26 kcal/mol by infrared spectroscopy^{21,22}). In order to gain some insight into the anisole problem we have previously studied this simpler case.

To save computation time we have carried out a full geometry optimization for different values of the dihedral angle $C_2C_1O_7C_8$ (ϕ) (from the planar to the orthogonal form) using the semiempirical INDO method²³ and the optimization procedure of Rinaldi et al.²⁴ The results obtained, shown in Figure 2a, are in very good agreement with the experimental ones. The planar conformation is predicted to be the most stable one, and the rotational barrier found is in very good accord with the experimental values. Using the INDO optimized geometry we have recalculated the corresponding potential curve, with a minimal STO-3G basis set. The results obtained (dashed line in Figure 2a) are similar to the semiempirical ones; though the rotational barrier (4.08 kcal/mol) is still in poorer agreement with the experimental value, it improves with respect to previous calculations.¹⁷

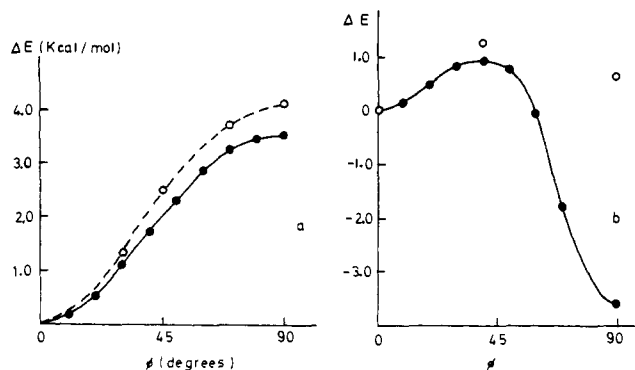


Figure 2. (a) Calculated rotational barrier for phenol. Full line corresponds to INDO results with fully optimized geometries for each value of ϕ . Dashed line corresponds to ab initio calculations, with a STO-3G minimal basis set, and the INDO optimized geometry. (b) INDO calculated rotational barrier for anisole with fully optimized geometries for each value of ϕ . Circles correspond to ab initio calculations (STO-3G basis) using the experimental geometry for each value of ϕ .

The corresponding 1s orbital energies were used to evaluate phenol proton affinities for different values of the dihedral angle. The PA value predicted using eq 2 for the planar conformation (194.0 kcal/mol) is in fairly good agreement with the experimental value⁵ (195.0 kcal/mol), but the important point is that the basicity of the para carbon atom decreases dramatically with the rotation of the -OH group. The value obtained for a dihedral angle of 45° is 188.6 kcal/mol and for the orthogonal conformation it is 184.6 kcal/mol.

One can expect anisole to behave in a similar way; therefore we have carried out ab initio calculations, using the STO-3G minimal basis set, for different values of the dihedral angle ϕ in anisole, keeping the remaining geometrical parameters unchanged and equal to those corresponding to the experimental geometry,¹³ finding that the orthogonal form, obtained in this way, is almost degenerate in energy with the planar form.

When the corresponding PA's are evaluated for different values of ϕ , using eq 2 and 3, we find a similar behavior to that of phenol and the intrinsic PA of the para carbon atom decreases to 187.5 kcal/mol for $\phi = 45^\circ$ and to 185.3 kcal/mol for the orthogonal conformation, and the basicity of the oxygen atom increases. Its intrinsic PA is 198.9 kcal/mol for $\phi = 45^\circ$ and 199.5 kcal/mol for $\phi = 90^\circ$, in good agreement with the experimental value⁵ (199.4 kcal/mol). Of course in phenol this is not an important point, since the planar conformation is the most stable one, but can be of importance in anisole, whose conformation is not definitively established.

One thing seems, however, clear: only one conformer of anisole must be stable, since ICR proton affinity values determined at 300 K⁴ are in good agreement with data obtained at 600 K.⁵ On the other hand, there is experimental evidence²⁵ that the rotational barrier of anisole is greater than that of phenol, and admitting that only one conformer is stable this can be explained in two ways: (a) The orthogonal conformation lies 3.61 kcal/mol above the planar one (with a potential curve similar to that of phenol). (b) The potential curve has the shape predicted by INDO calculations using fully optimized geometries for different values of ϕ (see Figure 2b) and with a rotational barrier higher than that of phenol and in good accord with the experimental value.

According to our results the first possibility is not likely to occur, since this would imply that (planar) anisole should exhibit a much smaller PA value than the experimental one.

We can therefore conclude that the linear relationship between 1s binding energies and proton affinities applies to the protonation of anisole. Protonation seems to depend on the

conformation of the methoxy group relative to the aromatic ring. According to our results, in the planar conformation anisole is a stronger base than phenol, and protonation can occur either on the ring or on the substituent. The rotation of the methoxy group increases the basicity of anisole, which behaves as an oxygen base. This fact could be responsible for the absence of deuterium exchange in anisole, pointed out by Beauchamp.⁶

Our results bring out, once more, the problem of the conformation of anisole and they ratify, to some extent, the INDO results, though no definitive answer can be given on this particular point. The full geometry optimization at the ab initio level, which would settle the question, would require the use of an optimization procedure similar to that employed to obtain our INDO results, which would be too expensive.

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An ab Initio Study of the Cis-Trans Photoisomerization of Stilbene

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Abstract: The molecular energies of the ground and lowest excited $\pi\pi^*$ states for the cis and trans isomers of stilbene and for the twisted geometry of the molecule have been evaluated by the SCF method followed by configuration mixing. The orbital basis is a minimal basis of STO/3G orbitals and the CI includes all relevant second-order interactions of the ground and lowest excited configurations. Two-term Fourier interpolations of the computed energies have provided potential energy curves along the coordinate of internal rotation. The potential curves support the adiabatic mechanism for the trans-cis thermal conversion in the ground state and for the sensitized photoconversion in the lowest triplet state and a nonadiabatic mechanism for the direct photoisomerization in the lowest excited singlet state.

Introduction

Several mechanisms have been proposed for the direct cis-trans photoisomerization of stilbene and of the related α,ω -diphenylpolyenes.^{2,3} Given the correlation diagram of the orbital levels in *cis*- and *trans*-stilbene (Figure 1), the isomerization reaction, after Woodward-Hoffmann,⁴ is allowed in the lowest excited B (S_1 , T_1) and A (S_2) states. The excitations to the B and A states are essentially described as $(4a) \rightarrow (4b)$ and $(4a)^2 \rightarrow (4b)^2$, respectively. An alternative description of the S_1 , T_1 , and S_2 states can be given in terms of biradicaloid states.⁵

Experimentally it has been possible to prove that the direct photoreaction does not follow the triplet pathway.³ Among the mechanisms involving states in the singlet manifold, it was first proposed that the optical excitation to the S_1 state is followed

by adiabatic motion on the S_1 energy curve to a minimum located at the twisted geometry ($\varphi = 90^\circ$) and by deactivation onto the ground potential energy surface. This mechanism contrasts with the results of a spectroscopic investigation⁶ where it was deduced that the S_1 state has in fact a barrier at $\varphi = 90^\circ$ high enough to make the state inactive in the photo-reaction. For this reason a second mechanism was postulated,⁷ where the molecule, before deactivation, undergoes a nonadiabatic crossing from the S_1 to the S_2 potential surface, which has a minimum at $\varphi = 90^\circ$.

The S_2 state, owing to its forbidden character, has not been observed by conventional one-photon spectroscopy. The overall experimental knowledge of the S_1 potential curve is also rather limited.

The validity of the one-electron model, on which the