

## Acidity Enhancement of the Cyclopentadiene Ring by PH<sub>2</sub> and AsH<sub>2</sub> Substitution\*

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**Abstract.** The intrinsic acidity of cyclopentadiene and its PH<sub>2</sub> and AsH<sub>2</sub> derivatives has been investigated at the B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p) level of theory. The calculated intrinsic acidity of cyclopentadiene is consistent with the available experimental data. Substitution of one of the H atoms of the C(sp<sup>3</sup>)H<sub>2</sub> group of cyclopentadiene by PH<sub>2</sub> and AsH<sub>2</sub> leads to a significant acidity enhancement of 44 and 34 kJ mol<sup>-1</sup>, respectively. This acidity enhancement is the result of the balance of two opposite effects: a) a decrease in the aromaticity of the anion on going from the unsubstituted to the substituted forms, b) the stabilization of the anion in the substituted derivatives, through an interaction of the π-cloud of the ring with the X–H bonding orbitals of the PH<sub>2</sub> or AsH<sub>2</sub> groups. This renders the interaction of the substituent with the five membered ring stronger upon deprotonation, as reflected in a strengthening of the C–P and the C–As bonds.

**Keywords:** acidity, gas-phase, cyclopentadiene derivatives, density functional theory

### INTRODUCTION

One of the most important achievements in the last half of the last century was the development of gas-phase ion chemistry.<sup>1</sup> The possibility of measuring the basicity and acidity of many chemical compounds in the absence of any interaction with the solvent provides a new vision of these chemical processes, because it was possible to measure the intrinsic reactivity of the systems.<sup>1,2</sup> One can say that this was the origin of a new chemistry, because in quite often the basicity or acidity trends observed in the gas phase were not only different to those observed in solution, but in many cases opposite. As a matter of fact, our previous knowledge on the basicity or acidity properties of the chemical compounds, was determined mostly by solvation, rather than by the intrinsic basicity or acidity of the system. Furthermore, the possibility of comparing gas-phase and solution magnitudes opened also the possibility of gaining more insight on solvation effects. Soon after the first measurements of gas-phase acidities and basicities were reported in the literature, a particular attention was focused on the characterization of superbases and superacids in the gas-phase,<sup>3</sup> with the final goal of finding a superacid able to transfer spontaneously a proton to a superbase, to finally produce an ion-pair in the gas-

phase. In this context, the contribution of theory to design and therefore to propose for their synthesis good candidates to behave as a superbase or as a superacid was crucial, and the efforts of the group of Zvonko Maksić were and still are remarkable.<sup>4–17</sup> They have actually proposed different ways to enhance the basicity or the acidity of a compound, profiting in some cases significant changes in the electron delocalization triggered by the protonation or the deprotonation of the system or combining these effects with the added stabilization caused by intramolecular hydrogen bonds.

In spite of the numerous papers devoted to analyze intrinsic basicities and acidities, many aspects governing these properties are not completely understood yet. In the last decade our group has devoted some efforts to investigate the influence of the substituents on the acidity or basicity of a given functional group. In particular we have shown that for primary amines, phosphines, arsines, silanes, germanes, thiols and selenols a huge increase of the acidity takes place when the heteroatom is bonded to an unsaturated moiety.<sup>18–23</sup> As a matter of fact this enhancement is particularly large for α,β-unsaturated derivatives, due to a strong stabilization of the anion produced upon deprotonation. It is well known that the cyclopentadiene ring possesses quite

\* Dedicated to Professor Zvonimir Maksić on the occasion of his 70<sup>th</sup> birthday.

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acidic hydrogens in the condensed phase<sup>24,25</sup> because the loss of a proton leads to a significant aromatization of the ring and, accordingly to a strong stabilization of the anion. The synthesis of unsubstituted cyclopentadienylphosphine and cyclopentadienylarsine and their characterization as non-aromatic systems have been recently reported.<sup>26</sup> However, the corresponding amino derivative has never been isolated, because it rearranges to yield the corresponding imine, also a kinetically unstable compound. The question we address in this work, through the use of high-level density functional (DFT) calculations, is whether the attachment of a PH<sub>2</sub> or AsH<sub>2</sub> substituent to the cyclopentadienyl moiety can lead to significant changes in its acidity, and whether the deprotonation is still favored from the five-membered ring.

## COMPUTATIONAL DETAILS

The geometries of cyclopentadiene, and its PH<sub>2</sub> and AsH<sub>2</sub> derivatives, as well as those of the different deprotonated species derived from these compounds have been optimized using the B3LYP method. This DFT approach combines the Becke's three-parameter non-local hybrid exchange potential<sup>27</sup> with the nonlocal correlation functional of Lee, Yang and Parr,<sup>28</sup> and it has been shown to provide reliable geometries for a wide variety of compounds,<sup>29-33</sup> with a rather good accuracy/cost ratio. The same approach has been used to obtain the structures of all possible deprotonated forms. For this purpose a 6-31+G(d,p) basis set was used, because the inclusion of diffuse functions is essential to get an adequate description of anions. The same functional has been shown to provide reliable gas-phase basicities and acidities,<sup>14,16,17,34-39</sup> provided that a flexible enough basis set is used. Hence, in our study final energies were obtained using the same functional together with a 6-311+G(3df,2p) basis set expansion. The harmonic frequencies of all the systems under investigation were obtained at the same level of theory used for the geometry optimizations in order to assess that all the stationary points found correspond to local minima of the potential energy surface and to calculate the contribution of the vibrational degrees of freedom to the thermal corrections.

The bonding in these systems has been analyzed by using three complementary approaches, namely the atoms in molecules (AIM) theory,<sup>40</sup> the electron localization function (ELF) theory<sup>41,42</sup> and the natural bond orbital (NBO) approach.<sup>43</sup> Within the framework of AIM theory we have located the bond critical points (bcp) of each compound, because the electron density at these points offers valid quantitative information on the strength of the bond. On the other hand, taking into account that as we mentioned above, the deprotonation

of these systems triggers an aromatization of the five-membered ring, an analysis of the ellipticity of the bond permits to follow the changes in its multiple bond character. This question can be also analyzed in terms of the weights of the different resonant structures contributing to the stability of the system, which can be obtained through the use of the natural resonance theory (NRT) in the framework of the NBO approach.<sup>43</sup> Furthermore, a second order perturbation analysis of the Fock matrix within the NBO scheme provides information on the interactions between occupied and empty molecular orbitals which may offer some insight into the factors contributing to stabilize or destabilize a given compound. The NBO approach, has been also employed to obtain the Wiberg bond orders (BO).<sup>44</sup> These calculations have been carried out with the NBO-5.0 suite of programs.<sup>45</sup>

ELF<sup>41</sup> is an alternative analysis of the electron density. The ELF function, conveniently scaled between [0,1], identifies regions of space where electron pairs are localized. In this paper an ELF value of 0.80 will be adopted to locate the different electron pair basins, some of which are lone-pairs, whereas the others are bonding pairs. Their populations and synaptic orders provide useful information on the bond characteristics. ELF grids and basin integrations have been computed with the TopMod package.<sup>46</sup>

## RESULTS AND DISCUSSION

The acidic site of cyclopentadiene is obviously the saturated carbon atom, because, as already mentioned, when one of the protons of this group is removed, the resulting anion becomes aromatic. For the particular case of the PH<sub>2</sub> and AsH<sub>2</sub> derivatives, all possible deprotonation processes have been considered. However, as expected, the loss of a proton from any of the CH groups of the five-membered ring is systematically very unfavorable with respect to the loss of the proton attached to the sp<sup>3</sup> carbon atom, or the loss of a proton from the substituent. Hence, in what follows only these latter two possibilities will be discussed in detail.

The structures of the neutral compounds and the most stable deprotonated forms are schematized in Figure 1. A more detailed information on these optimized geometries is provided in Table S1 of the supporting information. The total energies, thermal corrections to enthalpy and entropy values are given in Table S2 of the supporting information. In Table 1 we present the calculated acidities, measured as the negative of the enthalpy or the Gibbs free energy of the process:



**Table 1.** Intrinsic acidities ( $\Delta_{\text{acid}}H$  and  $\Delta_{\text{acid}}G$ ) of cyclopentadiene derivatives

Substituent	Deprotonated group	$\frac{\Delta_{\text{acid}}H_{\text{calc}}}{\text{kJ mol}^{-1}}$	$\frac{\Delta_{\text{acid}}H_{\text{exp}}}{\text{kJ mol}^{-1}}$	$\frac{\Delta_{\text{acid}}G_{\text{calc}}}{\text{kJ mol}^{-1}}$	$\frac{\Delta_{\text{acid}}G_{\text{exp}}}{\text{kJ mol}^{-1}}$
H	C(sp <sup>3</sup> )H	1478.2	1481. ± 9.2	1446.6	1455. ± 8.4
			1485. ± 12		1459. ± 8.4
			1479. ± 5.4		
PH <sub>2</sub>	PH <sub>2</sub>	1527.8		1494.5	
	C(sp <sup>3</sup> )H	1430.5		1397.9	
AsH <sub>2</sub>	AsH <sub>2</sub>	1485.6		1452.9	
	C(sp <sup>3</sup> )H	1444.2		1411.8	

It can be observed that for cyclopentadiene, which is the only compound for which the gas-phase acidity has been measured,<sup>47–49</sup> our theoretical estimate is always within the experimental error, although the agreement is better with the measurements of Bartmess *et al.*<sup>49</sup> This indicates that our estimated values for the PH<sub>2</sub> and AsH<sub>2</sub> derivatives should be considered reliable. It is also apparent from the values in Table 1 that the deprotonation of the substituent is unfavorable with respect to the loss of the proton attached to the same carbon atom, which, as in the case of the parent compound, leads to a significant aromatization of the system.

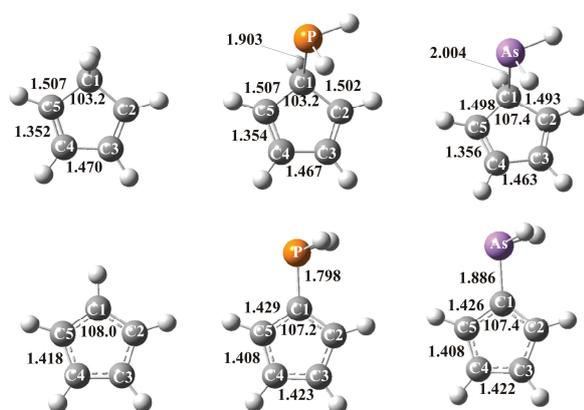
It is worth noting however that the gap between the acidities of these two groups decreases significantly on going from the PH<sub>2</sub> derivative, for which this gap is 97.3 kJ mol<sup>-1</sup>, to the AsH<sub>2</sub> derivative, where the gap becomes less than half (41.4 kJ mol<sup>-1</sup>). However, the most striking result is the significant acidity enhancement predicted on going from the parent compound to the PH<sub>2</sub> and AsH<sub>2</sub> substituted derivatives. More precisely, the replacement of one of the H atoms of the CH<sub>2</sub> of

cyclopentadiene by a PH<sub>2</sub> group implies an increase in the intrinsic acidity of the system of almost 50 kJ mol<sup>-1</sup>. This acidity enhancement is certainly smaller for the AsH<sub>2</sub> derivative but still significant (34 kJ mol<sup>-1</sup>). What is the origin of this acidity enhancement?

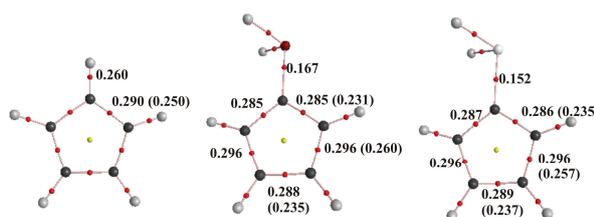
We have mentioned several times along this paper as a well established fact that the significantly large acidity of cyclopentadiene is due to the aromatization of the system upon deprotonation, which is clearly reflected in an equalization of the C–C distances within the five-membered ring (Figure 1), as well as in the equalization of the electron densities at the corresponding bcps. (Figure 2).

No doubt a certain aromatization of the system should be also expected when the PH<sub>2</sub> and AsH<sub>2</sub> derivatives lose the H attached to the C(sp<sup>3</sup>), as it is also mirrored in a certain equalization of the C–C bond distances within the ring (Figure 1). However, this aromatization seems not to be as complete as in the case of the parent compound. As shown in Figure 2, the electron density is preferentially accumulated in the two C2–C3 and C4–C5 bonds, C1 being the substituted carbon atom. This seems to indicate that a more localized structure is found for the anions of the PH<sub>2</sub> and the AsH<sub>2</sub> derivatives than for the unsubstituted parent anion. This is ratified by the increase in the ellipticity of these two bonds with respect to that in the parent anion, indicating that the C2–C3 and C4–C5 increase their double bond character. Concomitantly the other bonds undergo a decrease in their ellipticity with respect to the parent compound indicating a decrease in their double bond character, in other words the ring becomes less aromatic.

This description is completely consistent with that obtained through the use of the NRT theory (Figure 3), which shows that while for the parent anion all possible mesomeric forms contribute equally to the bonding of the system, for the PH<sub>2</sub> and AsH<sub>2</sub> derivatives, structure



**Figure 1.** B3LYP/6-31+G(d,p) optimized geometries of cyclopentadiene, its PH<sub>2</sub> and AsH<sub>2</sub> derivatives (top line) and their most stable deprotonated species (bottom line). Bond lengths are expressed in Å and bond angles in degrees.

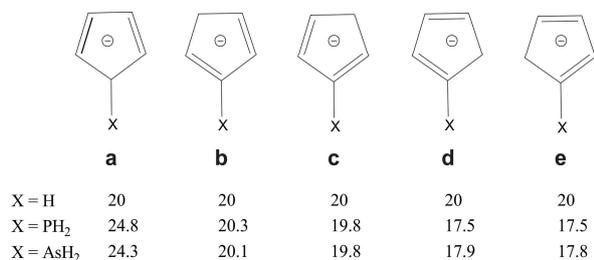


**Figure 2.** Molecular graphs of the deprotonated species of cyclopentadiene and their  $\text{PH}_2$  and  $\text{AsH}_2$  derivatives. Electron densities at the bond critical points are given in a.u. The values within parentheses correspond to the ellipticity of the bond.

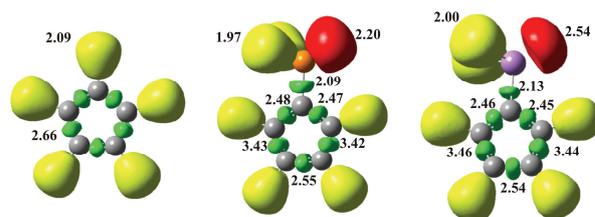
**a** (Figure 3) is dominant. This is in agreement with the fact that for these two compounds, the C2–C3 and C4–C5 bond orders (1.455) are greater than those of the other bonds in the ring (1.337 for the C1–C2 and C1–C5 bonds and 1.446 for the C3–C4 bond) and also larger than the C–C bond orders in the parent anion (1.403), and in line with the AIM results. This picture is also consistent with that obtained when the ELF theory is applied (Figure 4) which shows that on going from the parent compound to the  $\text{PH}_2$  and  $\text{AsH}_2$  substituted derivatives a significant accumulation of electrons takes place in the C2–C3 and C4–C5 basins, whose population changes from 2.66 to 3.43 and 3.46 respectively.

It seems clear then that the aromatic character should be smaller in the  $\text{PH}_2$  and  $\text{AsH}_2$  derivatives than in the parent compound. Indeed, when the nucleus independent chemical shift (NICS) is evaluated for these three anions 1.0 Å above the center of the ring, what is usually known as NICS(1), the values obtained (–9.58 ppm, –8.90 ppm and –8.90 ppm for cyclopentadiene and its  $\text{PH}_2$  and  $\text{AsH}_2$  substituted derivatives, respectively) indicate that cyclopentadiene anion is the most aromatic of the three. It seems then clear that the acidity enhancement observed upon substitution has to have a different origin.

A clue on the possible origin of the calculated acidity increase is provided by the ELF description,



**Figure 3.** Resonant structures contributing to the bonding in cyclopentadiene and their  $\text{PH}_2$  and  $\text{AsH}_2$  derivatives. The values correspond to the weight of the different forms expressed in percents.



**Figure 4.** Three-dimensional representations of ELF isosurfaces with  $\text{ELF} = 0.80$  for cyclopentadiene and their  $\text{PH}_2$  and  $\text{AsH}_2$  derivatives. Yellow lobes correspond to  $V(\text{C,H})$ ,  $V(\text{P,H})$  and  $V(\text{As,H})$  basins, red lobes correspond to  $V(\text{P})$  and  $V(\text{As})$  basins associated with P and As lone-pairs. Green lobes correspond to  $V(\text{C,C})$ ,  $V(\text{C,P})$  and  $V(\text{C,As})$  basins.

which indicates that the lone pair of the heteroatoms exhibit a quite large electron population, in both cases larger than 2.0. This points out to the ability of second and third-row atoms to accommodate excessive electron charge, due to the large size of their orbitals. This effect should be clearly greater for As than for P as clearly illustrated in Figure 4. However this is not the only factor behind the observed acidity enhancement. A second order perturbation NBO analysis shows the existence of a significant interaction between the  $\pi$ -system of the ring and the  $\sigma_{\text{XH}}$  bonding orbitals of the substituent, with interaction energies of about 28.0  $\text{kJ mol}^{-1}$ , and similar to that involved in a typical hyperconjugation effect. Due to a more effective overlap, this interaction is greater in the case of the  $\text{PH}_2$  than for the  $\text{AsH}_2$  derivative. At the same time in both derivatives there is also a significant interaction between the P or the As lone pair and the C1–C5  $\sigma^*$  antibonding orbital. Both effects contribute to reinforce significantly the interaction of the substituent with the five membered ring in the anionic form, which accordingly exhibits a C–P and a C–As bond distance much shorter than in the neutral form (Figure 1). Hence, although many arsines are usually more acidic than the corresponding phosphines,<sup>18,19</sup> the particular nature of the cyclopentadienyl substituent leads to two opposite effects resulting in a higher acidity for the cyclopentadienylphosphine.

## CONCLUSION

Our theoretical estimates on the intrinsic acidity of cyclopentadiene agree very well with the available experimental data. Although all the measured values are affected by a significant error, our estimates seem to support the more recent measurements of Bartmess *et al.*<sup>49</sup> Substitution of one of the H atoms of the  $\text{C}(\text{sp}^3)\text{H}_2$  group of cyclopentadiene by  $\text{PH}_2$  and  $\text{AsH}_2$  leads to a significant acidity enhancement, which for the P derivative is as large as 49  $\text{kJ mol}^{-1}$ , and a little smaller (34  $\text{kJ}$

mol<sup>-1</sup>) for the As derivative. An analysis of the bonding of the deprotonated species reveals that this acidity enhancement is the result of the balance of two opposite effects, a decrease in the aromaticity of the system on going from the unsubstituted anion to the substituted ones, which would result in an acidity dampening rather than in an acidity enhancement and the stabilization of the anion in the case of the PH<sub>2</sub> and AsH<sub>2</sub> derivatives, through an interaction of the  $\pi$ -cloud of the ring with the X–H bonding orbitals of the substituent and the interaction of the substituent lone pair with the closest C–C bond of the ring. As a consequence, the interaction of the substituent with the five membered ring becomes stronger upon deprotonation, as reflected in a strengthening of the C–P and the C–As bond.

*Supplementary Materials.* – Supporting informations to the paper are enclosed to the electronic version of the article. These data can be found on the website of *Croatica Chemica Acta* (<http://public.carnet.hr/cccaa>).

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## SAŽETAK

### Povećanje kiselosti ciklopentadienskog prstena supstitucijom s $\text{PH}_2$ i $\text{AsH}_2$

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Prirodna kiselost ciklopentadiena i njegovih  $\text{PH}_2$  i  $\text{AsH}_2$  derivata studirana je primjenom B3LYP/6-311+G(3df,2p)//B3LYP/6-31+G(d,p) nivoa teorije. Izračunata prirodna kiselost ciklopentadiena u skladu je s dostupnim eksperimentalnim podacima. Supstitucija jednog H atoma  $\text{C}(\text{sp}^3)\text{H}_2$  grupe ciklopentadiena s  $\text{PH}_2$  i  $\text{AsH}_2$  grupama dovodi do značajnog povećanja kiselosti od 44 i 34  $\text{kJ mol}^{-1}$  u istom slijedu. Ovo povećanje kiselosti rezultat je ravnoteže dva suprotna efekta: a) smanjenja aromatičnosti aniona idući od nesupstituirane prema supstituiranoj formi, b) stabilizaciji aniona u supstituiranim derivatima, interakcijom  $\pi$ -oblaka iz prstena sa X–H veznim orbitalama  $\text{PH}_2$  ili  $\text{AsH}_2$  skupine. Ovaj efekt povećava interakciju supstituenta s peteročlanim prstenom nakon deprotoniranja, što se odražava na jačanje C–P i C–As veza.