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Resonance Structures and Electron Density Analysis**

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bond order · electronic structure · hybridization · π bonding · resonance structures

The concept of resonance in chemistry is closely connected with Linus Pauling, who summarized the theoretical background in his book *The Nature of the Chemical Bond*.[1] He stressed that this theory does not aim to describe a physical domain, but mainly to simplify the chemical understanding of molecules and bonding, although a solid quantum-mechanical background came from the valence bond theory by Heitler and London.[2] In the theory of resonance, different electronic configurations combine to produce a molecular wave function, the energy of which is of course lower than that of the constituents. The idea of reference structures that merge together to produce a hybrid was also criticized because the reference structures cannot usually be isolated. In fact, Pauling restricted to a note Hückel's criticism that "at the best it [the theory of resonance] provides a picture which could be described no less accurately in other terms".[3]

The sensible use of experimental information on the molecular geometries to estimate the mixing of resonance structures was important in Pauling's approach. This approach allowed the definition of chemical bonding concepts, which are fundamental in modern organic chemistry. Since then, many applications have been proposed based on structural analysis within the framework of "resonant molecules", thus challenging molecular orbital (MO) theory.[4] In more recent times, the use of resonance concepts in the rationalization of the hydrogen bonding is notable.[5]

Additional experimental evidence could be used to estimate the mixing between electronic configurations, for example, the electron density $\rho(r)$, an observable which extends beyond the molecular geometry. Studies on $\rho(r)$ date back to the 1960's[6] and have often been nonroutine, until considerable developments occurred in X-ray diffraction (in particular, the availability of fast area detectors) and in computational chemistry (in particular, the enormous progresses of the density functional theory). Atomic charges, inter-atomic electron sharing, and intermolecular interactions can be computed from a theoretical or experimental $\rho(r)$ function.

Stalke and co-workers have analyzed the electron density in some organolithium complexes.[7] In a recent study,[8] they reported the coordination of picoline (PicH) and the picolyl anion (Pic) to Li to form [{PicPicHLi}$_2$] (PicLi; Figure 1). The coordination of Pic is particularly interesting as the electronic configuration of the anion is itself somewhat ambiguous. In fact, up to four reasonable resonance structures can be drawn (Scheme 1).

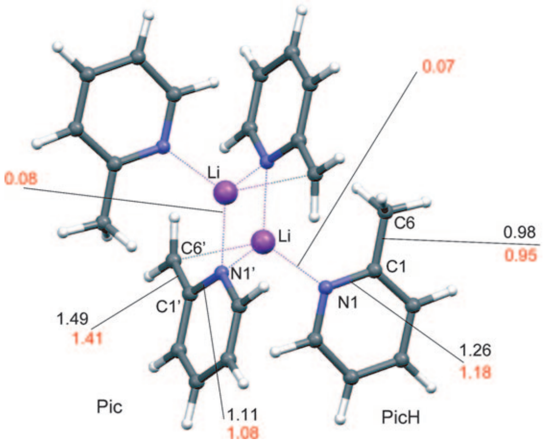
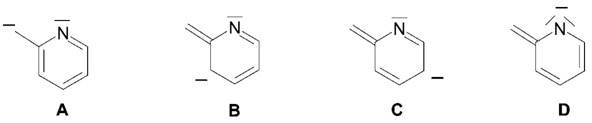


Figure 1. The PicLi complex. Delocalization indices are shown for selected bonds (Pic and PicH black, PicLi red).

How can we best represent this ligand? Stalke and co-workers discussed the experimental and theoretical evidence to ascertain whether a carbanion (**A**) or an enamide (**D**) is more appropriate. They analyzed the problem at various levels, starting from the molecular geometry up to the accurate distributions of $\rho(r)$, atomic charges, and electric potential [$\phi(r)$]. This study is valuable because the theoretical work is supported by challenging and accurate experimental results. However, in the present author's opinion, further analysis could be proposed for PicLi, which is an interesting



Scheme 1. Conceivable resonance structures of the picolyl anion (Pic).

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species that offers the possibility for comparison between the neutral and the anionic forms of the ligand.

What additional information can be gained from $\rho(r)$? Stalke and co-workers used the topology of $\rho(r)$, within the concept of atoms in molecules (AIM),[9] to estimate the bond order (BO), the atomic charges, and the hybridization of the pyridine nitrogen atom in PicH and Pic.

Is it possible to calculate the BO from $\rho(r)$? Bond orders are typically defined from molecular orbitals but derivation of the wavefunction from the experimental electron density is not possible. However, one can use $\rho(r)$ along a bond path (often just at the critical point that separates two bonded atomic basins) to empirically estimate the BO, by using reference single, double, and triple bonds as benchmarks.[9] While the procedure is popular, the reader should be aware that the electron density computed at a critical point only may not contain all the information on the chemical bonding. For example, a MO with a nodal plane that contains the bond path cannot contribute to $\rho(r)$ at the critical point. Nevertheless, a larger density is often considered a fingerprint of the double (or triple) BO character, because of π bonding (although π MOs cannot contribute to $\rho(r)$ at that point). This increased $\rho(r)$ reflects nothing more than a shorter interatomic distance. Contributions from a π-type MO are visible, instead, through the second derivatives of $\rho(r)$, which move away from the nodal plane. In fact, Stalke and co-workers analyzed the ellipticities[9] along the whole bond paths[10] to show the different bonding of the *o*-methyl carbon and the pyridine ring in PicH and Pic. In agreement with the molecular geometry, exocyclic C1–C6 in Pic has substantial anisotropy (hence, more π bonding).

The electron delocalization indices[11,12] (δ, which indicate the number of electron pairs shared by two atomic basins) are very useful in linking $\rho(r)$ and resonance structures.[13] Macchi and Sironi[13a] demonstrated that localized two-center two-electron metal–metal bonding does not take place in transition-metal carbonyl clusters, because some degree of delocalization with bridging, semibridging, or even nonbridging carbonyl groups always counteracts the direct metal–metal interaction.[14] They postulated an empirical link between δ and valence bond resonance structures. Martín Pendás et al.[13b] showed how the energy contributions of each resonance structure could be extracted once the interacting quantum atoms have been obtained (in AIM terms). Stalke and co-workers did not report δ values, which have been independently computed, for the present work, from wavefunctions at the same level of theory of reference [8] (Figure 1).[15] Interestingly, while in PicH, C1 and C6 share almost exactly one electron pair, in Pic $\delta(\mathrm{C1,C6}) \approx 1.5$, that is, a value larger than that for two adjacent carbon atoms in the pyridine ring (on average, $\delta \approx 1.3$). However, this bond cannot be regarded as a formal double bond, as the value of $\delta(\mathrm{C1,C6})$ is smaller than that of nonconjugated double bonds.[16] This difference gives an idea of the interference of resonance structure **A** (see Scheme 1). The larger $\delta(\mathrm{C1,C6})$ value causes a smaller $\delta(\mathrm{C1,N1})$ value in Pic, through the conjugation with the pyridyl ring. Upon complexation, the delocalization of electron pairs in the two ligands decreases, because polarization and partial charge transfer to Li cations affect the skeleton bonding. This is quite important, as the geometries of the free and the lithium-coordinated Pic are different. Stalke and co-workers did not explicitly consider the isolated Pic, but only PicH in its molecular-crystal form. Indeed, the geometry of the isolated Pic would more explicitly address the mixed character, which is less evident in PicLi.

The picture of resonance structures is completed after the analysis of atomic or group charges, for which Stalke and co-workers used natural bond orders (NBOs)[17] and the AIM charges.[9] The negative charge on the methylene group increases more than that of N1 upon moving from PicH to Pic. However, in the isolated PicH, N1 is already quite negatively charged, so the charge excess in the anion is accommodated in the rest of the molecule. The Laplacian $\nabla^2\rho(r)$, which typically addresses the hybridization of atomic orbitals, indicates a strong similarity between N1 atoms of PicH and Pic. In both examples, $\nabla^2\rho(r)$ around N1 is compatible with sp^2 hybridization, which favors structure **A** against structure **D**.[18] In this respect, the careful analysis by Gatti et al.[19] on nitranions can also be considered.

By considering all these results, we see that a $\rho(r)$ analysis provides a detailed description, which goes beyond molecular geometry, of PicLi. Some ambiguity remains because no particular configuration dominates, although the mixed character is confirmed by the analysis of δ values. The nature of the molecule is of course emphasized by the probe that is used to observe it, for example, its reactivity. Stalke and co-workers demonstrated that the $\phi(r)$ function explains the observed behavior of PicLi, in particular the typical electrophilic attack at the methylene group. It should be noted that the most negative region of $\phi(r)$ in Pic is around N1, but this drastically changes in PicLi,[8] where C6 is surrounded by the most negative potential and N1 is involved in the bonding to Li. Prediction of the chemical reactivity from the $\rho(r)$ distribution is certainly one of the ultimate goals of researchers in this field. The analysis in PicLi is facilitated by the dominant role of the charge control, whereas a more difficult task would be the prediction of soft (orbital-controlled) reactivity. This method requires a correlation between $\rho(r)$ and molecular polarizability, and represents the primary challenge for the next decade.

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