INDO Analysis of the Imidazole Anion and Hydrogen Addition Radicals

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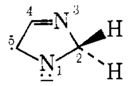
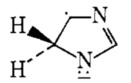
Abstract: The results of INDO calculations on two tautomeric forms of the imidazole anion radicals and of two H addition radicals of imidazole are presented. It is concluded that Kasai and McLeod[1] observed in fact the H addition radical on C5 of imidazole instead of the α-pyrrolenine form of the imidazole anion. Observations made with single crystals confirm this conclusion.

Kasai and McLeod[1] have reported the ESR spectrum of the imidazole anion radical generated within an argon matrix by the photoelectron transfer process. The spectrum is a large triplet of 50.0 G with a doublet splitting of around 15.0 G. They ascribed this spectrum to the tautomeric α-pyrrolenine form of the imidazole anion (IIa):

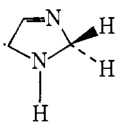


Ia

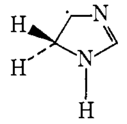


IIa

INDO calculations were also reported and taken as a further substantiation for the proposed assignment. On the other hand, Lamotte[2,3] has made a detailed ESR and ENDOR study of two H addition radicals observed after γ irradiation of imidazole single crystals:



Ib



IIb

In both, the ESR spectrum is a large triplet of around 50.0 G. However, the main radical produced by irradiation is radical Ib, resulting from H addition on C2; the concentration of radical IIb, resulting from H addition on C5, is much lower.[2] Contrarily to Kasai and McLeod,[1] Lamotte and Gloux[3] reported the failure of the INDO method to reproduce the experimental coupling constants.

In this note, we report INDO calculations[4] for the two possible tautomeric forms of the imidazole anion, Ia and IIa, and for the H addition radicals, Ib and IIb. The geometry of radical Ib has been improved compared to our previously published results.[5]

The four radicals were first calculated with the bond lengths and bond angles determined by X-ray crystallography[6] and with the methylene protons at tetrahedral angles to their neighboring atoms. As can be seen from Tables I and II the coupling constants are much higher than observed. The lengths of the bonds between the H addition site and the rest of the molecule were then varied. First consider radicals Ia and Ib in Table I. A strong reduction in the methylene proton coupling and, for the case of radical Ib, in the binding energy can be seen when the C–N bond length is increased from 1.35 to 1.40 Å. A further increase in the C–N bond length to 1.45 Å provokes a further decrease in the methylene proton coupling but also an increase in the binding energy. For a bond length of 1.40 Å the calculated coupling constants of the H addition to C2 are in good agreement with the experimental coupling constants[3] except for the sign of the coupling constant of the proton bonded to C4. It is unlikely that a fully optimized geometry would eliminate this discrepancy. Lamotte and Gloux[3] obtained too high methylene proton coupling constants and, therefore, very probably calculated the unperturbated molecule.

Similar behavior is observed for radicals IIa and IIb as can be seen in Table II. The unperturbated configuration gives bad agreement. The best agreement with the experimental coupling constants of Lamotte[2] is obtained with the following bond lengths: C–N, 1.40 Å and C–C, 1.50 Å. This configuration gives also the lowest binding energy that we obtained for this radical. These two bond lengths are also those giving best agreement between experimental and theoretical coupling constants for the H addition radicals of imidazole at C2 and of benzene.[5] The calculated methylene proton coupling constant of the anion radical IIa is much higher than the one observed by Kasai and McLeod,[1] whereas the proton bonded to C4 has a lower value. As stated by Kasai and McLeod,[1] the splitting of proton 4 is difficult to extract from the experimental spectrum since supplementary splittings are present. The calculated coupling constants of radical IIb are higher than those of radical IIa not only for proton 4 but also for proton 2. Moreover, the values of the binding energies of the anion radicals are always higher than those of the H addition radicals. Kasai and McLeod[1] have calculated radical IIa with the same structure as that of cyclopentadiene (C–C = C–N = 1.53 Å) and obtained: H(C5) = 50.0; H(C4) = 11.0; H(C2) = 2.0 G. Our series of calculations for radical IIa tends toward these values as the bond lengths are increased. However, energy consideration shows that the agreement is spurious. Therefore, very probably Kasai and McLeod[1] have in fact observed the radical resulting from H addition at C5 instead of a tautomeric form of the anion radical of imidazole.

These authors took account of the possibility that the radicals observed result from intermolecular transfer of hydrogen atoms but ruled it out because "only mild radiation was used to generate the radical anions, only a trace amount of atomic hydrogen was detected, and only one kind of radical was detected for each molecule".[1] Against the first point it may be argued that mild radiation conditions, i.e., dissociation of low-energy photoelectrons, do not preclude the generation of atomic hydrogen by photodissociation or dissociative electron attachment. As to the second point, it may be that there is a much higher probability of the dissociated hydrogen atoms adding onto neutral molecules instead of being trapped in the argon matrix. This is supported by the fact that deuterium atoms can be clearly detected. This effect is very probably due to the reduced mobility of deuterium atoms compared to hydrogen atoms.

Concerning the third objection, it has often been ob-

Table I. INDO Results for Different Geometries of the Imidazole Anion Radical Ia and of the H Addition Radical on C2 of Imidazole Ib[a]

Radical	N1	N3	H (C2)	H (C4)	H (C5)	H (N1)	Binding energy, au
Ia unperturbated	6.1	5.4	83.4	−1.2	−0.8		−3.9604986
Ia (C–N: 1.40 Å)	6.5	6.2	67.0	−1.1	−1.0		−3.9772743
Ia (C–N: 1.45 Å)	6.9	6.7	55.3	−1.2	−0.9		−3.9626721
Ib unperturbated	6.5	8.2	71.9	1.7	−5.0	−7.5	−4.0912715
Ib (C–N: 1.40 Å)	2.1	10.0	53.5	3.0	−7.3	−4.3	−4.2401173
Ib (C–N: 1.45 Å)	2.1	10.4	43.2	3.2	−7.6	−4.3	−4.2314298
Exptl (ref 3)			48.5	−2.3	−8.3	−5.4	

[a] Hyperfine splittings are given in gauss.

Table II. INDO Results for Different Geometries of the Imidazole Anion Radical IIa and of the H Addition Radical on C5 of Imidazole IIb[a]

Radical	N1	N3	H (C5)	H (C4)	H (C2)	H (N1)	Binding energy, au
IIa unperturbated	3.0	0.1	95.4	−9.1	−2.3		−3.9516016
IIa (C–N, 1.40 Å; C–C, 1.50 Å)	3.6	−0.2	67.7	−9.8	−2.8		−3.9646986
IIa (C–N, 1.45 Å; C–C, 1.50 Å)	3.7	−0.1	63.4	−9.9	−2.7		−3.9583209
IIb unperturbated	2.2	−3.6	80.6	−11.7	−9.1	−3.8	−4.2039454
IIb (C–N, 1.40 Å; C–C, 1.50 Å)	2.1	−3.7	52.4	−12.2	−9.9	−4.2	−4.2262218
IIb (C–N, 1.45 Å; C–C, 1.50 Å)	2.2	−3.7	50.0	−12.2	−9.9	−3.9	−4.2228873
Exptl (ref 1)			50.0	15.0			
Exptl (ref 2)			52.0	−16.0	−7.6	−3.1	

[a] Hyperfine splittings are given in gauss.

served in the solid state that the formation of H addition radicals is very specific. This can be seen from the overwhelmingly high concentration of radical Ib compared to that of radical IIb in single crystals of imidazole.[2] This has also been observed in single crystals of 1-CH_3-Cyt (Cyt is cytosine) where the H addition at C5 dominates the one at C6.[7] In naphthalene the H addition occurs at the α position.[8]

However, it is possible to obtain different relative concentrations of the various adducts. For example, in Cyt·H_2O crystals the main H adduct radical formed by irradiation at the C5=$\dot{\mathrm{C}}$6 double bond results from H addition at C5,[9,10] whereas, in Cyt·HCl crystals, the only H adduct radical at the C5=C6 double bond observed is the one resulting from H addition at C6.[11] A similar behavior is observed for crystals of 1-CH_3-Ur[12] (Ur is uracil) and 1-CH_3-Ur·HBr.[13] In the crystals of Cyt·HCl[11] and 1-CH_3-Ur·HBr,[13] the anion radicals of cytosine and 1-CH_3-Ur have been positively identified and observed to transform into H addition radicals. Therefore, it is conceivable that H addition via an anionic stage occurs at a position different from hydrogen addition to a neutral molecule. The Hückel MO method[14] seems to support this hypothesis. Indeed, to a good approximation, it is the carbon with the highest free valence and the highest net negative charge which will be the center of reactivity of a molecule;[15] this is carbon 5 in neutral cytosine and 1-CH_3-Ur, and carbon 6 in the anion radicals. For imidazole, it is C5 for the neutral molecule and C2 for the negatively charged molecule. All this lends support to our suggestion that Kasai and McLeod[1] first produced H atoms which subsequently add to the imidazole molecule at position 5. Following this argument through, the H addition radical on C2 observed in single crystals of imidazole[2,3] must be formed via an anionic stage.

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