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AB INITIO CALCULATIONS ON THE GROUND-STATE SYMMETRY OF THE 1-IMIDAZOLYL AND 1-PYRAZOLYL RADICAL

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Abstract—Geometry optimization by *ab initio* methods with a STO→3G basis set and a subsequent calculation with the 4–31G basis set indicates that 1-imidazolyl and 1-pyrazolyl radical both have $B_1(\pi)$-symmetry. The former has an $A_2(\pi)$-state at 0.50 eV, and a σ-state at 0.54 eV. The latter has an A_2-state at 0.23 eV and a metastable σ-state at 0.45 eV. If formed in the σ-state, 1-pyrazolyl may live long enough to react as a σ-radical. A limited CI has little effect, except that the A_2-states are coming down relatively to the other states. For both radicals the σ-state has a double minimum potential, even though in pyrazolyl the nitrogen atoms possessing the electron-deficient lone pair orbitals are neighbours.

INTRODUCTION

The 1-pyrazolyl radical was recently described by Janssen *et al.*[1] who found a simple way of generating it via a homolytic cleavage of the fairly easily accessible t-butyl-1-pyrazole percarboxylate. Its isomer, the 1-imidazolyl radical, was observed by Samuni and Neta,[2] after addition of OH-radicals to imidazole in water at pH 10–12. The adduct shows a slow elimination of water, in which the N-proton is involved, leading to the 1-imidazolyl radical. A similar procedure for pyrazole gave no elimination, and no 1-pyrazolyl radical. Imidazolyl radicals are proposed as intermediate in the oxidative phosphorylation, a key biological process.[3-5] For these radicals both a π-type and a σ-type ground state can be envisaged. Phenyl radicals are known to have the unpaired electron in a σ-type orbital,[6] but in the case of 1-imidazolyl and 1-pyrazolyl radical there is a definite possibility that the electron-rich π-system (6 π-electrons over 5 centers) will drop one electron into the σ-system, resulting in π-symmetry for the molecule. A similar situation holds, e.g. for amino radicals.

This so-called σ-π problem is drawing increasing attention. Koenig and Wielesek[7] have discussed it for the succinimidyl-radical, Richardson *et al.*[8] in their calculations on 1-pyrrolyl found a π-ground state with CNDO/2 and a σ-state with INDO. In 1-imidazolyl this situation has been investigated experimentally by Samuni and Neta.[2] Their EPR measurements strongly suggest a $B_1(\pi)$-ground state. Evleth *et al.*[9] however, based on INDO calculations suggested a $B_2(\sigma)$-state. The experimental data of Janssen *et al.*[1] for 1-pyrazolyl, although not decisive, supports a σ-type ground state. In a preliminary study of the imidazole radical[10] we reported an *ab initio* STO→3G geometry optimization. A simple argument shows why geometry optimization is absolutely essential. The highest occupied orbitals of each symmetry, one of which will be an electron short, have very different densities in space. The highest occupied σ-orbitals, a_1 and b_2 are localized. The highest occupied π-orbitals, b_1 and a_2, are strongly delocalized and have—different—specific bonding and antibonding regions in space. It is clear that very different geometries for the lowest state of each symmetry can be expected. By choosing an arbitrary geometry for a calculation there is a danger of putting one or other state at a disadvantage.

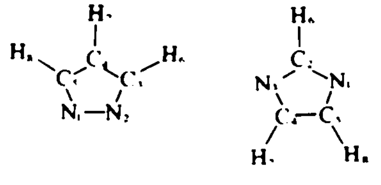

Fig. 1. The 1-pyrazolyl and 1-imidazolyl radical.

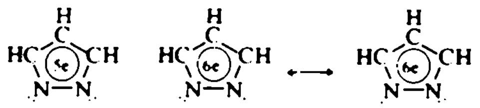

Fig. 2. The π- and σ-ground state of pyrazolyl.

As can be expected, the calculations result in two low lying π-states (B_1-ground state and the A_2-state at 0.36 eV) and a σ-state at higher energy. This state has a double minimum potential (Fig. 3), the minima lying at 0.63 eV. Qualitatively for pyrazolyl the prospects of a σ-ground state look better. A larger interaction between the nitrogen lone-pair orbitals may raise the highest σ-orbital, whereas the highest π-orbital (b_1) will be lower because of a larger contribution of the nitrogen p_z-orbitals (see Discussion).

CALCULATIONS

All calculations were performed using the IBMOL-programme.† IBMOL employs a Restricted Hartree–Fock operator; this operator was preferred to an Unrestricted Hartree–Fock operator of which the resulting eigenstates are contaminated by states of different multiplicity. As the amount of spin contamination is different for different states, a useful comparison becomes questionable. The geometry optimizations were carried out for both imidazolyl and pyrazolyl with a minimal STO→3G basis set.[11] At the minima found for each state we performed a calculation with the more flexible 4–31G basis set,[12] including limited configuration interaction.‡ The positions

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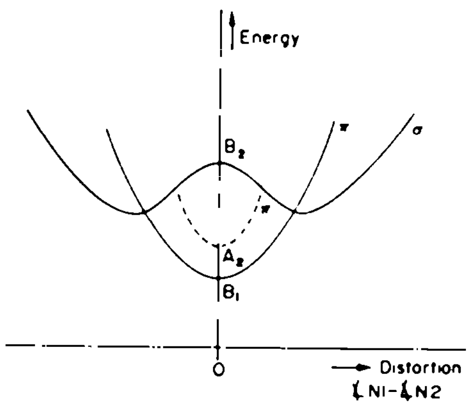

Fig. 3. General situation of order of states for 1-imidazolyl and 1-pyrazolyl radical.

of the H-atoms were optimized. All R(C–H) were varied simultaneously in an early stage, found to be 2.041 a.u. (1.080 Å), and kept in subsequent calculations. The H-atom is always near the bisector of the angle formed by the C atom it is attached to and both its neighbours. On optimizing the CCH-angles the deviation from this angle for H6 and H8 towards N2 and N1 in pyrazolyl respectively, and for H7 and H8 towards N3 and N1 in imidazolyl respectively was calculated several times and always found to be 4–6°. The minimal energy geometries for each state as well as the calculated energies at that point are given in Tables 1 and 2 under the heading of the appropriate state symmetry. At the geometry of the σ-state the energy of the π-state is given.

According to the SCF-calculations with the 4–31G basis set both imidazolyl and pyrazolyl are predicted to be $B_1(\pi)$-radicals. In imidazolyl there is an $A_2(\pi)$-state at 0.50 eV, and a lower symmetrical σ-state at 0.54 eV. In pyrazolyl there is an $A_2(\pi)$-state at 0.23 eV, and a metastable lower symmetrical σ-state at 0.45 eV.

Table 1. Imidazolyl

	σ	B_1	A_2	B_2
r(N1–C2)	2.561	2.765	2.569	2.546
r(C2–N3)	2.567			
r(N3–C4)	2.641	2.443	2.739	2.656
r(C5–N1)	2.635			
r(C4–C5)	2.577	2.838	2.553	2.576
∡ N1	110.9	102.3	104.3	109.9
∡ N3	105.1			
∡ C4	109.2	111.3	108.7	106.6
∡ C5	106.0			
∡ C2	108.8	112.9	114.0	107.0
Energy STO→3G	221.3195	−221.3427	−221.3295	221.2969
4–31G	223.7854	−233.8051	223.7866	223.7630
after CI	−223.8127	−223.8304	223.8192	223.7895†
π-state energy STO→3G	221.3158			
4–31G	−223.7888			
after CI	223.8164			

distances: 1 a.u. = 0.529167 Å
energies: 1 a.u. = 27.21 eV = 627.2 kcal/mole

†For both imidazolyl and pyrazolyl the CI for B_2 was performed on non-symmetrically converged eigenvectors (see text).

Table 2. Pyrazolyl

	σ	B_1	A_2	B_2
r(C5–N1)	2.597	2.451	2.745	2.561
r(N2–C3)	2.567			
r(C3–C4)	2.674	2.751	2.611	2.655
r(C4–C5)	2.614			
r(N1–N2)	2.548	2.789	2.460	2.415
∡ N1	116.6	108.1	110.7	110.7
∡ N2	102.5			
∡ C3	110.7	110.3	107.5	106.7
∡ C5	102.5			
∡ C4	107.7	103.2	103.7	105.3
Energy STO–3G	221.3120	−221.3282	−221.3213	221.2881
4–31G	−223.7671	223.7835	223.7752	223.7552
after CI	223.7968	−223.8129	223.8173	223.7834†
π-state energy STO–3G	221.3032			
4–31G	−223.7644			
after CI	223.7939			

†For both imidazolyl and pyrazolyl the CI for B_2 was performed on non-symmetrically converged eigenvectors (see text).

In imidazolyl at the geometry of the A_2-minimum the B_1-state is calculated to have E = − 223.7833 a.u., i.e. only 2 kcal/mole higher than the A_2-state. The relative stabilities of the other states will be discussed later.

As expected, the optimized geometries for the different symmetries are very different. For imidazolyl our predictions are in accordance with Samuni's experimental results. For pyrazolyl our results offer a challenge to record and interpret the EPR-spectrum. It may be very complicated as pyrazolyl radicals in both the B_1- and A_2-state may occur. Short-lived radicals in the σ-state having coupling constants an order of magnitude larger than those in the π-states may disturb the spectra even further.

CI; *the* A_2-B_1 *problem.* As we wanted to be sure that no dominant effect was neglected in the SCF-results, a small-scale CI was decided upon. The CI-programme employed does not make use of symmetry. For planar systems, calculated in C_s-symmetry this impediment can easily be dealt with. There is however a problem with the B_2-state. Convergence of the SCF-calculation in C_s-symmetry leads to an incorrect wave function. We will come back to this point in the Discussion. Here it should be mentioned only that the CI-calculations were performed using these—lower-symmetrical—orbitals: the resulting energy gain was subtracted from the correct C_{2v}-SCF solution. About 50 configurations were selected, arising from single and double excitations out of six high-lying occupied orbitals: one b_1, one a_2, three σ and the singly occupied orbital, and into five virtual orbitals: one b_1, one a_2, one σ describing C–H excitation and a σ-orbital describing ring σ-bond excitation and again the singly occupied orbital. The improvement of the ground state originates mainly from the interaction with configurations in which relative to the ground configuration $\pi\pi \rightarrow \pi^*\pi^*$ excitation has occurred (65%). After CI, the A_2-states have come down relative to the B_1-states. In fact in pyrazolyl the A_2-state ends up below the B_1-state. This is possible because of the extreme proximity of the two orbitals as well as the two configurations in this system. The states will probably turn out to be within 0.1 eV of each other. As a result the ground state of 1-pyrazolyl is predicted to contain two π-state minima with vibrational interconversion.

DISCUSSION

The highest occupied molecular orbitals. In cyclopentadienyl π_2 and π_3, representing an orbital of e-symmetry in D_{5h}, and a_2 and b_1 in C_{2v}, are degenerate. $(CH)_3(N)_2$ is isoelectronic, the orbitals still possess approximately D_{5h}-symmetry, but the N atoms have a much larger effective nuclear charge for π-electrons and bind these more strongly. In imidazolyl the b_1-orbital almost has nodes at the N atoms and the a_2-orbital has large coefficients there, so it is not surprising that b_1 is the higher π-orbital. In pyrazolyl the b_1- and a_2-orbitals have coefficients of about the same magnitude on nitrogen and almost equi-energetic π-states can be anticipated.

However, the interaction between π (necessarily b_1) and the b_1-orbital originating from the D_{5h} e_1''-pair, will push this last orbital above its a_2-partner, thus causing both the pyrazolyl- and the imidazolyl ground states to be $B_1(\pi)$-states.

The highest σ-orbitals are the lone-pair atomic orbitals on nitrogen. They split to form a symmetric (n_+) and an antisymmetric (n_-) combination. It may not be immediately clear which of the two will be in the higher position, and will be one electron short. Two types of interactions are known to play a role: through-space and through-bond.[13] The common through-space interaction is governed by overlap. It tends to favor n_- with respect to n_+, as long as the overlap between the lone pair atomic orbitals is positive. Through-bond interaction is governed by the symmetry properties of the LUMO and the HOMO of σ-symmetry. The σ-LUMO and the σ-HOMO often have opposite symmetry; if one will favour n_- the other disfavours n_-, and *vice versa.* Through-space and through-bond interactions are of about the same magnitude.

A very good example is found in the series pyrazine (1,4-diazabenzene), pyrimidine (1,3-diazabenzene), pyridazine (1,2-diazabenzene). In these molecules the σ-HOMO is symmetric, antisymmetric and symmetric respectively with respect to the mirror plane that interconverts the nitrogen line pairs. It thus disfavours n_-, n_- and n_+. The σ-LUMO with respect to this plane is antisymmetric, symmetric and antisymmetric respectively, favouring n_-, n_+ and n_-. The measured ionization potentials (I.P.'s) of σ-symmetry and the assignments for pyrazine are 9.4 eV (n_+) and 11.4 eV (n_-);[14] for pyrimidine 9.7 eV (n_-) and 11.2 eV (n_+);[15] and for pyridine 9.3 eV (n_-) and 11.3 eV (n_+).[16] In this last case the through-space interaction—never to be neglected—dominates. Interestingly, this delicate balance of effects can be reproduced very well by *ab initio* methods, whereas CNDO grossly overestimates the through-bond interaction.[17] With Koopmans' theorem the correct ordering of I.P.'s is found, and the calculated splittings are in fairly good agreement with experiment, as is shown by Clementi's[18] and Palmer *et al.*[19] minimal basis set calculations, giving $n_- - n_+$ splittings of 2.5, + 1.5 and + 2.6 eV. In split-shell calculations Almlöf *et al.*[20] give splittings of 2.6, + 1.6 and + 2.2 eV, and report improved values upon applying corrections to Koopmans' theorem. Our radicals can be thought to arise from the diazabenzenes by removal of a CH-fragment (consequently, a π-state is obtained).

During geometry optimization of imidazolyl and pyrazolyl we found the A_1-state, in which the n_+-combination is one electron short at least 1.5 eV above the B_2-state. We decided not to optimize the geometry of this state. According to our expectations it should have a C_{2v}-minimum.

The double minimum potential. When the nuclear coordinates possess C_{2v}-symmetry, converged calculations on the B_2-radicals in C_s-symmetry show a special feature. Induced by rounding-off errors in the computer, a lower-symmetrical solution is formed which proves to be slightly lower in energy. The electrostatical force exerted on the nuclei accordingly force these to a lower-symmetrical structure.

It is important to notice that the lower-symmetrical solution for the C_{2v}-nuclear skeleton does not correspond to physical reality; one can easily see that upon going from one σ-well to the other, the first derivative of the energy is not continuous near the peak. The occurrence of the lower-symmetrical solution only INDICATES that a distortion can be expected.

In C_{2v} each nitrogen lone pair orbital has about 1.5 electrons. The extra π-electron can be thought of as being divided equally over both N atoms. Distortion results in a situation with one nitrogen possessing roughly one electron in its lone pair orbital and two π-electrons, and one nitrogen possessing two electrons in its lone pair orbital and one π-electron, thus avoiding intramolecular charge transfer for this neutral radical species.

Seen in this way, the origin of this surprising feature is hybridization. The high symmetrical radical has a particularly unfortunate hybridization; after distortion the molecule possesses one pyridine-type nitrogen and one pyrrole-type nitrogen. For π-radicals no such distortion is found, as was checked by calculations; both N atoms are pyridine-like. As has been established in our previous communication, such a double-minimum potential is not due to an artefact, like, e.g. the double-minimum potential found with a minimal basis set and a RHF-operator for allyl radical.[21] A larger basis set and a CI-calculation still show a double-minimum potential for the σ-radicals.

The distortion must be found at the N atoms involved, and leads to differences in bond angles. The differences between the $\measuredangle$N can be understood as differences in (N-) lone pair-bond repulsions or an increase in 2s-character for the completely filled lone pair orbital and a decrease in 2s-character for the half-filled lone pair orbital. These bond angle differences could be slightly larger for the radicals than for the parent system. We calculated $\measuredangle N1 - \measuredangle N2 = 14.1°$ for pyrazolyl, mean experimental 7.8° in pyrazole, and calculated semi-empirically by angle strain minimization $-7°$;[22] we calculated $\Delta N1 - \Delta N3 = -5.8°$ for imidazolyl, mean experimental $-3.0°$ in imidazole, calculated semi-empirically $-3°$.[22] In view of this, our calculated distortions are probably somewhat too large. In the SCF-calculations with the 4–31G basis set the magnitude of the peak for the double-minimum potential of the σ-radical amounts to 14.1 kcal/mole for imidazolyl and 7.5 kcal/mole for pyrazolyl. If the magnitude of the distortion has been exaggerated in the STO–3G optimization, the barrier will be somewhat higher.

An equivalent way of describing the asymmetric σ-state is as a localized hole state. Bagus and Schaefer[23] performed calculations on the O_2^+-ion in which one 1s-electron is missing. Only when the symmetry element connecting the O atoms (inversion) was destroyed for the total wave function, satisfactory agreement with ESCA-results could be obtained. The missing 1s-electron then derives exclusively from one of the O atoms. Jonkman[24] found that He_2^+ should be described as a localized hole state if the internuclear distance is larger than 2.8 a.u. (the equilibrium distance for this species is 2.1 a.u.). Jonkman ascribes the origin of this effect to orbital polarization. Also the $n \rightarrow \pi^*$ excited states and n-cations of pyrazine[25] and benzoquinone[26-28] are examples of localized hole states. The measurement of a dipole moment in the latter case demonstrates the lower symmetry. A distortion of the D_{2h}-nuclear skeleton has not been found yet,[29] although, according to our opinion, it must be present.

Stability of the σ-states. Finally we turn to the question whether these radicals can exist in σ-symmetry. We suppose that the radical is formed by homolytic cleavage of a covalent bond. A decreasing number of electrons in the nitrogen π-lone pair orbital is correlated with increasing planarity. For reasons of conjugation the N atom in pyrrole is most probably coplanar, and replacing of one more CH-fragment by a N-atom, no doubt further increases the stability of the planar form. The transition state of the homolytic cleavage is then coplanar, the radical is formed as a σ-radical. This σ-radical must resemble imidazole or pyrazole rather closely. Indeed there is agreement between the calculated geometry for the σ-radicals and the experimental data for the parent systems, measured for pyrazole by microwave,[30] X-ray,[31,32] and neutron diffraction,[33] and for imidazole by X-ray.[34,35]

In imidazolyl, at the geometry of the σ-well, the π-state is lower and the σ-radical will undergo decay instantaneously. In pyrazolyl at the geometry of the σ-well the σ-state is lower.

When in Fig. 3 the energy curve for the σ-state is moved upwards so that the well in it is higher than the π-state at this point, the actual situation for imidazolyl is represented. In order to represent pyrazolyl in Fig. 3, the $B_1(\pi)$-curve must be moved upwards. It should be noted, however, that the resulting energy differences are small: in the order of magnitude of a few kcal/mole (Tables 1 and 2).

As indicated earlier, the optimization with the minimal basis set exaggerated the distortion, as a result the well will be deeper than calculated. It is important to notice that the C_{2v} geometries of the B_2- and each of the π-states are rather different. To visualize this one imagines in Fig. 3 the B_1-geometry (the molecule is more broad and flat) in front, the B_2-geometry in the plane of the paper and the A_2 geometry (the molecule is more tall and slim) behind it. Near the σ-well the energy of the π-state must be roughly constant for a geometry change which in Fig. 3 corresponds to a direction perpendicular to the paper; this coordinate will contain a barrier between the A_2- and the B_1-like states. We mentioned the equivalence in geometry of the radical and the parent molecule: there is probably only very little ring-vibrational energy present in the radical after dissociation. If this excess energy stays out of the N-angle distortion coordinate, it is not at all unlikely that the reactive 1-pyrazolyl radical is able to react in the time it lives as a σ-radical. This conclusion: pyrazolyl behaves at the chemical time scale as a metastable σ-radical, supports Janssen's experimental data: N-phenylpyrazole is a major end-product after homolytic cleavage at 150°C of t-butyl-1-pyrazole-percarboxylate in benzene.

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