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Molecular and Electronic Structure of the Low-Lying Electronic States of the 1-Pyrazolyl and 1-Imidazolyl Radicals[†]

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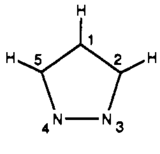
Abstract: Results of ab initio calculations (at the ROHF and CISD levels of theory) on the low-lying electronic states of 1-pyrazolyl and 1-imidazolyl radicals are reported. In addition to the electronic ground state, which is predicted to be a π-type doublet of B_1 symmetry, both radicals have a π- and a σ-type excited doublet state of A_2 and B_2 symmetry, respectively. Due to the fact that the single-configuration electronic wave functions of the $^2A_2$ and $^2B_2$ states are subject to Hartree–Fock instability, asymmetric planar structures (C_s) are of lower energy than the symmetric (C_{2v}) ones at the ROHF level for these states. At the optimum geometry of the σ-type radical ($^2B_2$), the ground-state π-type radical ($^2B_1$) is calculated (Davidson-corrected CISD) to lie about 18 kcal/mol (1-pyrazolyl) and 6 kcal/mol (1-imidazolyl) above the σ-type radical. In agreement with an earlier theoretical study and experimental findings, the present results suggest that, although the ground state is a π-type doublet, on the chemical time scale 1-pyrazolyl can behave as a metastable σ-type radical if it is generated in the excited $^2B_2$ state.

Determination of the electronic ground states of 1-pyrazolyl (**1**) or its isomer 1-imidazolyl (**2**), free radicals derived from the homolytic cleavage of the N–H bond of *N*-pyrazole (**3**) and *N*-imidazole (**4**), respectively, presents a fascinating challenge to the computational chemist. Assuming that **1** and **2** have C_{2v} symmetry, the unpaired electron may reside either in a σ-type orbital arising from combination of the two nitrogen nonbonding σ orbitals (i.e., **5** and **6**) or in a π-type orbital involving all five ring atoms (i.e., **7** and **8**). In the former case the radical is referred to as a "σ-type" radical, and in the latter as a "π-type" radical. These two classes of radicals are expected to have quite different physical and chemical properties.[1] While the σ-type radicals are expected to have a reactivity closely analogous to monocyclic aryl radicals like phenyl, the π-type radicals can a priori be compared with amino radicals.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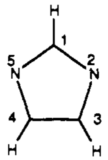
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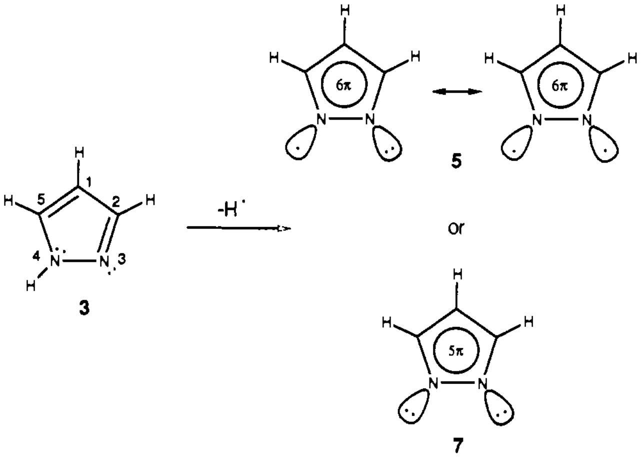
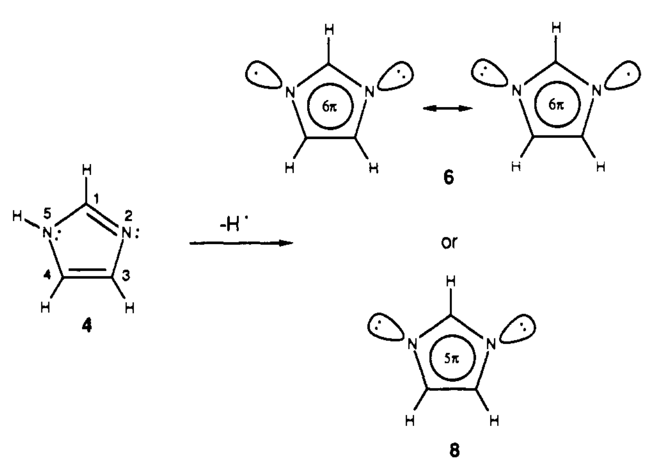


Free radical **1** has been proposed by Janssen et al.[2] as an intermediate either in the thermal decomposition of *tert*-butyl-1-pyrazole percarboxylate in benzene solution at 140 °C or in the photolysis of 1-nitropyrazole also in benzene solution. On the basis of the exclusive formation of 1-phenylpyrazole, which involves an electrophilic attack of benzene by **1** leading to an aromatic substitution, Janssen et al. conclude that **1** is a more aryl-like radical (i.e., has a σ-type ground state). Obviously, an ESR spectrum of **1** would be conclusive about its electronic structure but, to the best of our knowledge, it has not been recorded yet.



As regards **2**, imidazolyl radicals are proposed as intermediates in the oxidative phosphorylation, a key biological process.[3] Samuni and Neta[4] have generated **2** by addition of OH radicals to **4** in water at pH 10–12. Their ESR measurements strongly suggest a π-type ground state.

Evleth et al.[5] reported the first MO calculations on **2** in 1973 using the INDO method and, surprisingly, the electronic ground state was predicted to be a σ-type doublet of $^2B_2$ symmetry. Later ab initio calculations, using a rather modest (about 50 configurations) configuration interaction (CI) with the 4-31G basis at the STO-3G-optimized geometries, by Mulder and van der Meer[6] on the ground-state symmetry of radicals **1** and **2** predicted two low-lying π-type doublet states of B_1 and A_2 symmetry. At the self-consistent field (SCF) level of theory with the 4-31G basis set, the B_1 doublet was found to be the ground state in both free

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[‡] On leave of absence from the C.S.I.C.

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Table I. Calculated and Experimental Geometric Parameters for 1*H*-Pyrazole and 1*H*-Imidazole[a]

1*H*-Pyrazole[b]

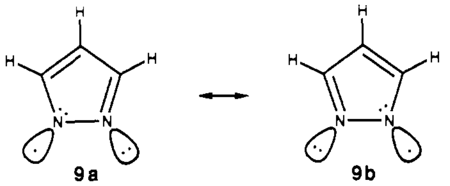
method	C_1C_2	C_1C_5	C_2N_3	C_5N_4	N_3N_4	$C_2C_1C_5$	$C_1C_2N_3$	$C_1C_5N_4$	$C_2N_3N_4$	$C_5N_4N_3$
HF/3-21G	1.419	1.363	1.313	1.353	1.379	105.0	111.8	107.1	104.5	111.6
HF/6-31G*	1.413	1.363	1.302	1.341	1.330	103.9	111.7	106.6	104.9	112.8
exptl[c]	1.416	1.372	1.331	1.359	1.349	104.5	111.9	106.4	104.1	113.1

1*H*-Imidazole[d]

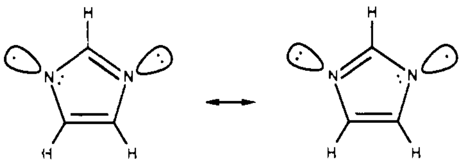
method	C_1N_2	C_1N_5	N_2C_3	N_5C_4	C_3C_4	$N_2C_1N_5$	$C_1N_2C_3$	$C_1N_5C_4$	$N_2C_3C_4$	$N_5C_4C_3$
HF/3-21G	1.300	1.368	1.394	1.385	1.353	111.1	106.3	107.1	109.7	105.9
HF/6-31G*	1.289	1.349	1.371	1.372	1.350	112.2	105.3	106.8	110.5	105.2
exptl[e]	1.314	1.364	1.382	1.377	1.364	112.0	104.9	106.9	110.7	105.5

[a] Distances are in angstroms and angles in degrees. [b] Atom numbering refers to **3**. [c] Reference 20. [d] Atom numbering refers to **4**. [e] Reference 21.

radicals. After CI the A_2 doublets came down relative to the $^2B_1$ states, so that the former became the ground state in the case of **1**. However, since the $^2B_1$–$^2A_2$ energy difference was calculated to be only 2.8 kcal/mol, the ground state of **1** was predicted to contain two minima with vibrational interconversion. Furthermore, a σ-type doublet of B_2 symmetry was found for **1** and **2**, lying at 18.5 and 25.7 kcal/mol, respectively, above the $^2B_1$ state. Curiously, such a σ-type doublet showed a double-minimum potential energy, so its equilibrium geometry was predicted to be a planar structure of C_s symmetry ($^2A'$ state) with one short bond (C_1C_2 in **1** and C_1N_2 in **2**) and one long bond (C_1C_5 in **1** and C_1N_5 in **2**) relative to structure of C_{2v} symmetry ($^2B_2$ state). The electronic structure of these asymmetric molecular geometries can be depicted as one of the two valence bond structures **9a** or **9b** and **10a** or **10b**, respectively.

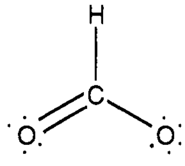


9a **9b**



10a **10b**

Taking into account the open-shell nature of the wave functions describing the various electronic states of **1** and **2**, the prediction of an asymmetric planar structure for the equilibrium geometry of the σ-type state is at least questionable. Mulder and van der Meer noted the obvious analogy that exists between the double-minimum potential predicted for the latter state of **1** and **2** and that calculated for allyl radical at the restricted open-shell Hartree–Fock (ROHF) level of theory,[7] which has been shown to be a computational artifact due to so-called "doublet instability" phenomenon.[8] This phenomenon, a particular case of the most general Hartree–Fock instability problem,[9] is characterized by broken symmetry solutions of the ROHF equations at symmetric geometries (i.e., an energy lowering is observed if the MOs are allowed to become asymmetric), with a concomitant prediction of unequal bond lengths. Such a spurious bond length alternation compensates for the inadequacy of the spin-restricted single-configuration wave function in providing correlation between electrons of opposite spin. However, on the basis that the aforementioned CI calculations still predicted a double-minimum potential for the σ-type state of **1** and **2**, Mulder discarded the possibility that the asymmetric molecular geometry determined for this state could be ascribed to such a phenomenon. In this regard it should be noted that in the conceptually related case of the formyloxyl radical (**11**) McLean et al.[10] have recently shown that the asymmetric equilibrium geometry, with unequal CO bond lengths, calculated in earlier studies for the σ-type state ($^2B_2$) is a consequence of the deficiencies in the theoretical model used to include the electron correlation effects.



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An interesting result of potential value in understanding the chemistry of **1** that emerges from the theoretical study of Mulder and van der Meer is that at the minimum geometry of the σ-type state, the $^2B_1$ state lies about 2 kcal/mol higher in energy. On the basis of this result, the authors postulated that if **1** is formed in the σ-type state, it may live long enough to react as a σ-type radical before decaying to the lowest π-type state. This hypothesis might account for the aforementioned experimental findings of Janssen et al. However, it should be noted that the calculated σ–π vertical energy difference ($\approx$2 kcal/mol) seems too small to give a reasonable support to the above hypothesis.

In summary, we feel that the conclusions drawn from the ab initio calculations of Mulder and van der Meer concerning the equilibrium molecular geometry of the σ-type doublet and the energy separation between the π- and σ-type states of **1** and **2** merit further study. To this end, here we report the results of additional high-level ab initio calculations on the molecular and electronic structure of the low-lying electronic states of 1-pyrazolyl and 1-imidazolyl radicals, in a continued effort to understand the chemical behavior of these interesting free radicals.

Computational Methods and Results

Single-configuration SCF-MO calculations on doublet free radicals may be performed by using the spin unrestricted (UHF)[11] or spin restricted (ROHF)[12] Hartree–Fock procedures. Preliminary calculations on the low-lying doublet states of **1** and **2** indicated that the UHF wave functions are heavily contaminated by higher spin states. Consequently, the ROHF procedure of Davidson[13] was adopted to perform the SCF calculations of these doublet states. All ROHF calculations employed the GAMESS program package.[14]

Regarding the atomic basis set to calculate the equilibrium geometries, the relatively small split-valence 3-21G basis[15] ap-

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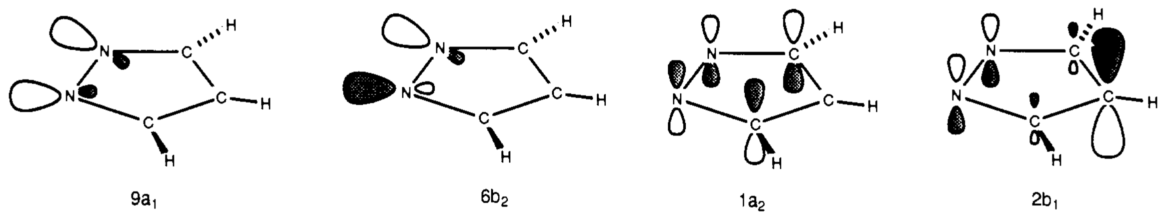
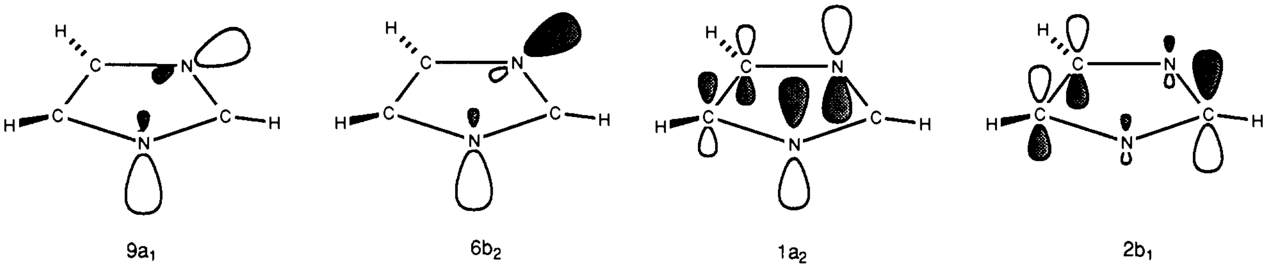


$9a_1$ $6b_2$ $1a_2$ $2b_1$

Figure 1. Qualitative drawings of the atomic orbitals that make the largest contribution to the $9a_1$, $6b_2$, $1a_2$, and $2b_1$ molecular orbitals of the 1-pyrazolyl radical.



$9a_1$ $6b_2$ $1a_2$ $2b_1$

Figure 2. Qualitative drawings of the atomic orbitals that make the largest contribution to the $9a_1$, $6b_2$, $1a_2$, and $2b_1$ molecular orbitals of the 1-imidazolyl radical.

peared to be the best choice because of its wide use in modern ab initio calculations of medium-size neutral molecules comprising first-row elements.[16] To assess the reliability of this basis set in the particular case of the heterocyclic species **1** and **2**, complete geometry optimizations at the SCF level were carried out on the parent closed-shell heterocycles **3** and **4**, employing a locally modified version[17] of the GAUSSIAN-80 system of programs.[18] The equilibrium geometries obtained with the 3-21G basis set are compared in Table I with those calculated with the more reliable split-valence plus d-polarization 6-31G* basis set[19] and with the experimental structures derived from microwave spectroscopy.[20,21] Although the geometrical parameters obtained by using the 6-31G* basis set are generally somewhat better, the values calculated with the 3-21G basis are reasonably close to experiment. For **3** the largest absolute deviations from experiment of the 3-21G-optimized geometrical parameters are 0.03 Å in the N_3N_4 bond length and 1.5° in the $C_5N_4N_3$ bond angle. In the case of **4** the largest absolute deviations from experiment are 0.012 Å in the bond length N_2C_3 and 1.4° in the $C_1N_2C_3$ bond angle. Taking into account these results, it was decided to use the 3-21G basis set to optimize the molecular geometries of the low-lying doublet states of **1** and **2**, rather than the much more computer-time-consuming 6-31G* basis.

The equilibrium geometries of the low-lying electronic states of **1** and **2** were initially optimized, within appropriate molecular symmetry constraints, with the semiempirical MNDO method[22] employing the MOPAC[23] program package and then further optimized at the ROHF level with the 3-21G basis set by the variable metric method of Murtagh–Sargent,[24] using analytically calculated forces. The 3-21G-optimized structures were characterized by their harmonic vibrational frequencies as minima, saddle points, or higher extrema, from the Cartesian force constants matrix calculated numerically by finite differences of analytical gradients.[25]

To obtain more reliable relative energies, additional single-point calculations were carried out with the larger split-valence 6-31G basis set[26] and with the 6-31G* basis set. To incorporate the effects of the valence-electron correlation on the relative energy ordering of the calculated electronic states, CI was used at the ROHF/3-21G optimum geometries with the 6-31G basis set. The CI calculations utilized the graphical unitary group approach (GUGA) of Brooks and Schaefer[27] as implemented in GAMESS. The CI wave function included all Hartree–Fock interacting[28,29] singly and doubly excited configurations (CISD) relative to the SCF reference configuration. The number of configurations varied from 26 398 for the $^2A_2$ states to 53 532 for the $^2A'$ states. The contribution to the correlation energy from quadruple excitations was obtained by using Davidson's formula to estimate the energy correction due to the effect of unlinked clusters (simultaneous pair correlation).[30] CI calculations including the latter energy correction will be referred as CIDVD.

Our best ab initio relative energies, denoted [CIDVD/6-31G*], were estimated by assuming additivity of the d-polarization functions and correlation energy (Davidson-corrected CISD) effects.[31] This procedure has been shown[32] to give a reliable approximation to the vastly more computer-time-consuming CI calculations with the 6-31G* basis set.

Finally, to obtain spin density distribution data that would be useful in aiding the identification of free radicals **1** and **2** by ESR spectroscopy in the near future, the spin densities at the nuclei were determined from the UHF wave functions calculated with the 6-31G* basis set for each ROHF/3-21G-optimized structure of C_{2v} symmetry.

The first step in the present investigation was to find out the possible low-lying electronic states of **1** and **2** before performing the corresponding theoretical calculations. Assuming C_{2v} molecular symmetry, there are four possible classes of doublet states, namely, A_1, A_2, B_1, and B_2. At the ROHF level of theory with

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Table II. Relevant Geometric Parameters[a] of the ROHF/3-21G Optimum Molecular Structures for Several Electronic States of the 1-Pyrazolyl and 1-Imidazolyl Radicals

1-pyrazolyl[b]

state	C_1C_2	C_1C_5	C_2N_3	C_5N_4	N_3N_4	$C_2C_1C_5$	$C_1C_2N_3$	$C_1C_5N_4$	$C_2N_3N_4$	$C_5N_4N_3$
$^2B_1$	1.454	1.454	1.282	1.282	1.500	102.4	111.4	111.4	107.4	107.4
$^2A_2$	1.378	1.378	1.443	1.443	1.274	104.8	109.3	109.3	108.4	108.4
$^2A''$	1.430	1.342	1.416	1.458	1.278	104.7	108.8	109.3	108.5	108.8
$^2B_2$	1.400	1.400	1.357	1.357	1.230	106.0	105.2	105.2	111.8	111.8
$^2A'$	1.414	1.378	1.335	1.354	1.325	105.9	111.1	103.5	103.1	116.3

1-Imidazolyl[c]

state	C_1N_2	C_1N_5	N_2C_3	N_5C_4	C_3C_4	$N_2C_1N_5$	$C_1N_2C_3$	$C_1N_5C_4$	N_2C_4	$N_5C_4C_3$
$^2B_1$	1.385	1.385	1.305	1.305	1.480	112.9	105.0	105.0	108.5	108.5
$^2A_2$	1.333	1.333	1.461	1.461	1.325	114.8	104.8	104.8	108.2	108.2
$^2A''$	1.461	1.269	1.343	1.463	1.330	113.8	105.5	102.0	109.6	109.1
$^2B_2$	1.328	1.328	1.395	1.395	1.347	105.3	111.4	111.4	105.9	105.9
$^2A'$	1.362	1.308	1.380	1.395	1.359	107.7	111.3	107.6	103.0	110.4

[a] Distances are in angstroms and angles in degrees. [b] Atom numbering refers to **1**. [c] Atom numbering refers to **2**.

Table III. Calculated Total Energies (hartrees) for Several Electronic States of the 1-Pyrazolyl and 1-Imidazolyl Radicals[a]

state	ROHF/3-21G	ROHF/6-31G	ROHF/6-31G*	CISD/6-31G	CIDVD/6-31G
			1-Pyrazolyl		
$^2B_1$	−222.862 84	−224.023 24	−224.138 96	−224.449 32	−224.509 98
$^2A_2$	−222.852 85	−224.018 79	−224.137 25	−224.446 33	−224.506 91
$^2A''$	−222.853 81	−224.019 78	−224.137 92	−224.445 91	−224.506 18
$^2B_2$	−222.835 34	−223.999 26	−224.110 41	−224.435 18	−224.496 33
$^2A'$	−222.847 54	−224.010 57	−224.119 64	−224.431 30	−224.490 57
			1-Imidazolyl		
$^2B_1$	−222.896 42	−224.059 44	−224.184 80	−224.481 43	−224.539 75
$^2A_2$	−222.870 65	−224.029 18	−224.142 94	−224.454 36	−224.514 86
$^2A''$	−222.884 31	−224.041 93	−224.156 98	−224.460 55	−224.519 96
$^2B_2$	−222.847 37	−224.004 86	−224.115 42	−224.445 35	−224.508 53
$^2A'$	−222.870 77	−224.028 99	−224.137 50	−224.446 03	−224.504 37

[a] All calculations at the ROHF/3-21G-optimized geometries.

the 3-21G basis set the electronic ground state of both free radicals is found to be a doublet of B_1 symmetry possessing five π electrons; its valence electronic configuration can be written as in (1).

$$(4a_1)^2(3b_2)^2(5a_1)^2(6a_1)^2(4b_2)^2(7a_1)^2(8a_1)^2(5b_2)^2 \\ (1b_1)^2(9a_1)^2(6b_2)^2(1a_2)^2(2b_1)^1 \quad {}^2B_1 \quad (1)$$

Simple qualitative pictorial descriptions of the four highest occupied MOs of **1** and **2** are shown in Figures 1 and 2, respectively. It is worth noting that the $9a_1$ and $6b_2$ MOs are, respectively, the in-phase and out-phase combinations of nitrogen nonbonding σ orbitals. The low-lying excited electronic states of **1** and **2** can be obtained by singly occupying the energetically similar $9a_1$, $6b_2$, and $1a_2$ MOs. Thus, promotion (relative to configuration 1) of a $1a_2$ electron to the $2b_1$ orbital gives rise to a second doublet state with five π electrons of A_2 symmetry, which can be written in short form as in (2). Excitation (relative to configuration 1) of a $6b_2$ electron to the $2b_1$ orbital yields a doublet state of B_2 symmetry possessing six π electrons, written as in (3).

$$...(9a_1)^2(6b_2)^2(1a_2)^1(2b_1)^2 \quad {}^2A_2 \quad (2)$$

$$...(9a_1)^2(6b_2)^1(1a_2)^2(2b_1)^2 \quad {}^2B_2 \quad (3)$$

In contrast to the $^2B_1$ and $^2A_2$ states, which are π-type doublets, the latter is a σ-type doublet. Finally, excitation (relative to configuration 1) of a $9a_1$ electron to the $2b_1$ orbital gives rise to a second σ-type doublet with six π electrons possessing A_1 symmetry, written as in (4).

$$...(9a_1)^1(6b_2)^2(1a_2)^2(2b_1)^2 \quad {}^2A_1 \quad (4)$$

The most relevant geometrical parameters of the ROHF/3-21G-optimized molecular structures obtained for the $^2B_1$, $^2A_2$, and $^2B_2$ states of **1** and **2** are summarized in Table II. For both radicals the $^2A_1$ state was found to lie very high in energy above the ground state, and therefore it was decided to omit its study.

The harmonic vibrational analysis proved the optimized structures obtained for the $^2B_1$ states to be true potential energy minima. In contrast, the optimized structures obtained for the $^2A_2$ states showed either one or two imaginary frequencies. These were associated with a normal mode of b_2 symmetry in **1**, and two normal modes of b_2 and a_1 symmetry, respectively, in **2**. The normal mode of b_2 symmetry suggested a concerted shortening and lengthening of the two equivalent C_1C_2 and C_1C_5 bonds in **1** (or C_1N_2 and C_1N_5 in **2**) breaking the C_{2v} molecular symmetry and leading to a planar structure (C_s symmetry) with unequal bond lengths. In fact, subsequent geometry reoptimization (at the ROHF/3-21G level) within the C_s symmetry constraints of the calculated $^2A_2$ structures, slightly modified according to the nuclear displacements indicated by the b_2 normal mode of imaginary frequency, yielded in each case a potential energy minimum. The most relevant geometrical parameters of these asymmetric π-type states ($^2A''$) are given in Table II.

Analogously, the optimized structures obtained for the $^2B_2$ states showed two imaginary frequencies associated with normal modes of b_2 and a_1 symmetry. A C_s-constrained geometry reoptimization (at the ROHF/3-21G level) of the $^2B_2$ structures, slightly modified according to the nuclear displacements indicated by the b_2 normal mode of imaginary frequency, led again in each case to a potential energy minimum, showing one short and one long C_1X (X = C or N) bond relative to the C_1X distances calculated for the $^2B_2$ state. The most relevant geometrical parameters of these asymmetric σ-type states ($^2A'$) are given in Table II.

The total and relative energies calculated at the different levels of theory are shown in Tables III–V. Finally, the spin densities at the nuclei and ^1H hyperfine coupling constant ratios for the $^2B_1$, $^2A_2$, and $^2B_2$ states of **1** and **2** are shown in Table VI.

Discussion

Geometrical Structures. The substantial geometrical differences found between the $^2B_1$, $^2A_2$, and $^2B_2$ states of **1** and **2** can be easily rationalized on the grounds of the different nodal planes of the singly occupied MOs (see Figures 1 and 2). Thus in the case of the $^2B_1$ states, the lenghtening of the N_3N_4 (C_3C_4) and shortening of the C_2N_3 and C_5N_4 (N_2C_3 and N_5C_4) bond distances in **1** (in

Table IV. Calculated Relative Energies (kcal/mol) for Several Electronic States of the 1-Pyrazolyl and 1-Imidazolyl Radicals[a]

state	ROHF/3-21G	ROHF/6-31G	ROHF/6-31G*	CISD/6-31G	CIDVD/6-31G	[CIDVD/6-31G*][b]
			1-Pyrazolyl			
$^2B_1$	0	0	0	0	0	0
$^2A_2$	6.3	2.8	1.1	1.9	1.9	0.2
$^2A''$	5.7	2.2	0.7	2.1	2.4	0.9
$^2B_2$	17.3	15.1	17.9	8.9	8.6	11.5
$^2A'$	9.6	8.0	12.1	11.3	12.2	16.3
			1-Imidazolyl			
$^2B_1$	0	0	0	0	0	0
$^2A_2$	16.2	19.0	26.3	17.0	15.6	22.0
$^2A''$	7.6	11.0	17.5	13.1	12.4	18.9
$^2B_2$	30.8	34.3	43.5	22.6	19.6	28.8
$^2A'$	16.1	19.1	29.7	22.2	22.2	32.8

[a] All calculations at the ROHF/3-21G-optimized geometries. [b] Estimated assuming additivity of the electron correlation and d-polarization functions corrections.

Table V. Total Energies (hartrees) of the $^2B_1$ State of the 1-Pyrazolyl and 1-Imidazolyl Radicals Calculated at the ROHF/3-21G-Optimized Geometry of the $^2B_2$ State[a]

molecule	ROHF/6-31G	ROHF/6-31G*	CISD/6-31G	CIDVD/6-31G	[CIDVD/6-31G*][b]
1	−223.98035 (11.9)	−224.10281 (4.8)	−224.39910 (22.6)	−224.45691 (24.7)	(17.6)
2	−224.01185 (−4.4)	−224.13184 (−10.3)	−224.43099 (9.0)	−224.48890 (12.3)	(6.4)

[a] The energies (kcal/mol) of the $^2B_1$ state relative to the $^2B_2$ are given in parentheses. [b] Estimated assuming additivity of the electron correlation and d-polarization functions corrections.

Table VI. UHF/6-31G*-Calculated Spin Densities (au) at the Nuclei and ^1H Hyperfine Coupling Constant Ratios for Several Electronic States of the 1-Pyrazolyl and 1-Imidazolyl Radicals[a]

1-Pyrazolyl[b]

	spin densities					$a(H_1)/a(H_2)$
state	C_1	C_2	N_3	H_1	H_2	
$^2B_1$	0.1824	−0.1222	0.1587	−0.0230	0.0114	2.02
$^2A_2$	−0.1159	0.1445	0.0144	0.0123	−0.0198	0.62
$^2B_2$	0.0354	0.0261	0.5451	−0.0067	0.0030	2.23

1-Imidazolyl[c]

	spin densities					$a(H_1)/a(H_2)$
	C_1	N_2	C_3	H_1	H_2	
$^2B_1$	0.1607	−0.1026	0.0952	−0.0211	−0.0169	1.25
$^2A_2$	−0.1402	0.1799	−0.0109	0.0156	−0.0024	6.50
$^2B_2$	−0.1169	0.0959	0.0473	0.0004	−0.0026	0.15

[a] All calculations at the ROHF/3-21G-optimized geometries. [b] Atom numbering refers to **1**. [c] Atom numbering refers to **2**.

2), as compared with those calculated for **3** (for **4**) (see Table I), are a consequence of a π-electron loss from a MO of **3** (of **4**), becoming the singly occupied $2b_1$ MO of **1** (of **2**), which is N_3N_4 (C_3C_4) bonding and C_2N_3 and C_5N_4 (N_2C_3 and N_5C_4) antibonding. Analogously, in the $^2A_2$ states, the lengthening of the C_2N_3 and C_5N_4 (N_2C_3 and N_5C_4) and shortening of the N_3N_4 (C_3C_4) bond distances in **1** (in **2**), as compared with those calculated for **3** (for **4**), are traced back to the loss of a π-electron from a MO of **3** (of **4**), becoming the singly occupied $1a_2$ MO of **1** (of **2**), which is C_2N_3 and C_5N_4 (N_2C_3 and N_5C_4) bonding and N_3N_4 (C_3C_4) antibonding. On the other hand, since the $^2B_2$ states have the same number (i.e., six) of π-electrons as the corresponding closed-shell parent molecules **3** and **4**, the ring bond distances in these states are expected to be close to those calculated for such molecules. In comparing Tables I and II, it is readily seen that this is true in the case **2**, but for **1** a substantial shortening is noticed of the N_3N_4 bond distance (1.230 Å) as compared to the value (1.379 Å) calculated for **3**. Again this result is easily understood by taking into account that the $6b_2$ MO of **1** has a nodal plane between the nitrogen atoms and, therefore, the single occupation of this orbital should reduce its negative contribution to N–N bonding.

As regards the asymmetric (C_s) structures $^2A''$ and $^2A'$, obtained from geometrical distortion of the symmetric (C_{2v}) structures $^2A_2$ and $^2B_2$, the question naturally arises as to what is the true equilibrium geometry of the second π-type ($^2A_2$) and the first σ-type ($^2B_2$) states of **1** and **2**. According to the energy differences between the C_{2v} and C_s structures calculated at the CIDVD level of theory (see Table III), it appears that the true equilibrium geometry of the latter states should be of C_{2v} symmetry. In our opinion, the appearance of lower energy C_s structures for these states at the single-configuration SCF level of theory is due to the aforementioned "doublet instability" phenomenon shown by the ROHF wave functions of $^2A_2$ and $^2B_2$ symmetries. To illustrate this point, single point ROHF/3-21G calculations at the C_{2v} optimized geometries of the $^2A_2$ and $^2B_2$ states were performed starting with a guess wave function of C_s symmetry. The SCF procedure converged to "broken-symmetry" (C_s) wave functions of lower energy than the conventional "symmetric" (C_{2v}) ones. Thus, in the $^2A_2$ state the energy lowering was 0.1 kcal/mol for **1** and 1.3 kcal/mol for **2** and in the $^2B_2$ state was 0.8 and 10.9 kcal/mol, respectively. These results indicate that in both radicals the "doublet instability" of the Hartree–Fock wave function is stronger for the $^2B_2$ state, as compared to the $^2A_2$. Furthermore, in the case of **1** the "doublet instability" of the ROHF wave function of the $^2A_2$ state is so weak that the small electron correlation furnished by its UHF wave function leads to the disappearance of the broken-symmetry solution. In fact, as the case in allyl radical,[33] it was found that the UHF/3-21G-optimized structure for the $^2A_2$ state of **1** is a true equilibrium geometry (zero imaginary harmonic vibrational frequencies). In contrast, as in the case in formyloxyl radical,[34] we have found that the UHF/3-21G-optimized structure for the $^2B_2$ state of **1** still has one imaginary frequency associated with a normal mode of b_2 symmetry. These results suggest that the amount of electron correlation that should be included in the SCF wave function of a given doublet state, to avoid the broken-symmetry solutions, depends critically on the existence of nonbonded electron pairs on the atoms formally bearing the odd electron in this state. It is worth noting that McLean and co-workers[10] have recently showed in the case of formyloxyl radical that it is necessary to use a multiconfiguration SCF (MCSCF) wave function including 1944 configurations to predict an unequivocal symmetric structure (C_{2v}) for the σ-type doublet ($^2B_2$).

Finally, since it has been mentioned above that the σ-type state ($^2B_2$) of **1** can be chemically relevant, we emphasize that the present CISD results (see Table III), in contrast to the smaller CI calculations by Mulder and van der Meer,[6] clearly indicate that an appropriate MCSCF treatment, similar to the afore-

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(33) See: Cook, D. B. *J. Chem. Soc., Faraday Trans. 2* **1986**, *82*, 187.
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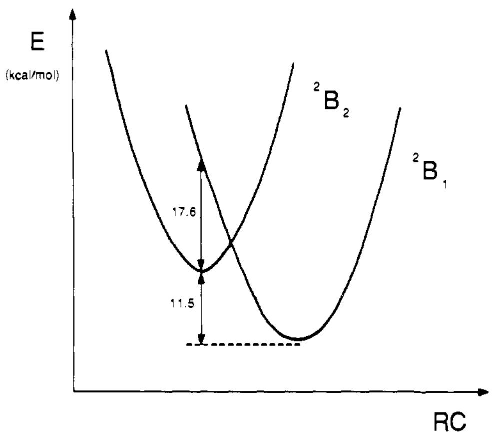

Figure 3. Schematic representation of the crossing between the potential energy surfaces of the $^2B_2$ and $^2B_1$ states of the 1-pyrazolyl radical along an arbitrary C_{2v} reaction coordinate.

mentioned for the same state of formyloxyl radical, should predict a symmetric (C_{2v}) structure for this state. Restrictions imposed by the size of the present molecule and the limitations of computer sources have prevented the use of such a MCSCF wave function to confirm this point.

Relative Energy of the Electronic States of 1-Pyrazolyl Radical. According to the present calculations, at the RHOF level of theory with the 6-31G basis set (see Table IV), the π-type doublet of B_1 symmetry is predicted to be the electronic ground state of **1**. At this level, the next electronic state is another π-type doublet of A_2 symmetry, lying only 2.8 kcal/mol above the $^2B_1$ state. However, both d-polarization functions and energy correlation effects reduce the $^2B_1$–$^2A_2$ energy difference; thus at the estimated CIDVD/6-31G* level of theory the difference is only 0.2 kcal/mol. The CI calculations of Mulder and van der Meer[6] predicted the $^2A_2$ state to lie 2.8 kcal/mol *below* the $^2B_1$. Since at present highest level of theory the calculated energy difference (0.2 kcal/mol) is less than the intrinsic error of the computational method employed, it is difficult to conclude which one of the π-type states is the ground state of **1**. In this regard it is worth noting that the calculated (see Table VI) ^1H hyperfine coupling constant ratios for the $^2B_1$ and $^2A_2$ states (2.02 and 0.62, respectively) suggest that *the ESR spectrum of **1**, should be conclusive in assigning the symmetry of the electronic ground state.*

The σ-type state ($^2B_2$), at the estimated CIDVD/6-31G* level of theory, is predicted (see Table IV) to lie 11.5 kcal/mol above the $^2B_1$ state. The CI calculations of Mulder and van der Meer[6] predicted a $^2B_1$–$^2B_2$ energy difference of 18.5 kcal/mol. The relatively small adiabatic energy difference predicted by the present higher level calculations and the fact that both states are well separated geometrically (e.g., the optimum N_3N_4 bond lengths differ by 0.27 Å) suggest that at the optimum geometry of $^2B_2$, the $^2B_1$ state may lie higher in energy. In fact, at the estimated CIDVD/6-31G* level of theory, the latter state is calculated (see Table V) to lie at 17.6 kcal/mol above the optimum structure of $^2B_2$. Therefore, it turns out that a crossing between the potential energy surfaces of these states must occur at some intermediate geometry lying higher in energy than the equilibrium geometry of $^2B_2$. Such a surface crossing is schematically illustrated in Figure 3. It follows that the present results give strong support to the aforementioned hypothesis of Mulder and van der Meer, namely, *if **1** is formed in the $^2B_2$ state* (e.g., by homolytic cleavage of N–H bond of **3**, *it can live long enough to react as a σ-type radical before decaying to the ground-state π-type radical.* As noted by the latter authors, the experimental findings of Janssen et al.[2] are consistent with this theoretical prediction.

Relative Energy of the Electronic States of 1-Imidazolyl Radical. In good agreement with Samuni and Neta's[4] interpretation of the ESR spectrum of **2**, the present calculations (see Table IV) predict the π-type doublet of B_1 symmetry to be the electronic ground state. In sharp contrast to the case of **1**, at all levels of theory the $^2A_2$ state of **2** is predicted to lie clearly above the $^2B_1$. At the estimated CIDVD/6-31G* level of theory the $^2B_1$–$^2A_2$ energy difference is calculated to be 22.0 kcal/mol. This value is about 3 times larger than that (7.0 kcal/mol) calculated by Mulder and van der Meer[6] using a smaller CI with the 4-31G basis set.

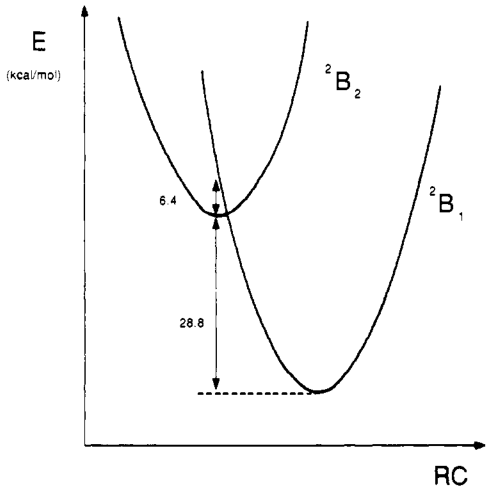

Figure 4. Schematic representation of the crossing between the potential energy surfaces of the $^2B_2$ and $^2B_1$ states of the 1-imidazolyl radical along an arbitrary C_{2v} reaction coordinate.

The calculated (see Table VI) ^1H hyperfine coupling constant ratio for the electronic $^2B_1$ state (1.25) is in excellent agreement with the experimental value of 1.29 reported by the latter authors. In this regard, it is worth noting that despite the higher spin state contamination shown by the UHF wave function of the low-lying electronic states of **1** and **2**, it appears that the Fermi contact analysis based on such a wave function can lead to correct predictions. This conclusion strengthens the above-mentioned suggestion that the ESR spectrum of **1**, complemented with the UHF/6-31G* calculated ^1H hyperfine coupling constant ratios for the $^2B_1$ and $^2A_2$ states, should lead to an unequivocal assignment of its electronic ground-state symmetry.

The σ-type state ($^2B_2$), at the estimated CIDVD/6-31G* level of theory, is predicted (see Table IV) to lie 28.8 kcal/mol above the ground state ($^2B_1$). The CI calculations of Mulder and van der Meer[6] predicted a $^2B_1$–$^2B_2$ energy difference of 25.7 kcal/mol. Such a large adiabatic energy separation suggest that at the optimum geometry of $^2B_2$, the $^2B_1$ state still may lie lower in energy. However, at the present highest level of theory, the latter state is calculated (see Table V) to lie at 6.4 kcal/mol above the optimum structure of $^2B_2$. At first sight it seems, therefore, that if **2** is generated in the $^2B_2$ state (e.g., by homolytic cleavage of the N–H bond of **4**), it should not undergo instantaneous decay to the ground-state π-type radical. However, the rather small vertical $^2B_2$–$^2B_1$ energy separation (6.4 kcal/mol) calculated at the optimum geometry of $^2B_2$ and the fact that from the geometrical point of view both states are relatively close (e.g., the optimum C_3C_4 bond lengths differ by 0.13 Å) suggest that the crossing between the corresponding potential energy surfaces must occur at some intermediate geometry lying close to the equilibrium geometry of $^2B_2$. Such a surface crossing is schematically illustrated in Figure 4. The chemically relevant prediction here is that *if **2** is generated in the excited $^2B_2$ state, it seems unlikely that it may live long enough to behave chemically as a metastable σ-type radical before decaying to the ground-state π-type radical.* This prediction is consistent with the experimental findings of Samuni and Neta.[4]

Conclusions

In this paper, results of ab initio calculations have been reported for the three lowest-lying electronic states of 1-pyrazolyl and 1-imidazolyl radicals. Analysis of the results suggests several points of potential value in understanding and interpreting the chemisry of these free radicals.

(1) The ground state of both radicals is calculated to be a π-type doublet. In addition, there is another π-type and a σ-type ($^2B_2$)

doublet lying low in energy. While in 1-imidazolyl radical the symmetry of the ground state is clearly predicted to be $^2B_1$, in the case of 1-pyrazolyl radical the calculated small (0.2 kcal/mol) energy difference between the two low-lying π-type states ($^2B_1$ and $^2A_2$) precludes a conclusive symmetry assignation. However, the calculated ^1H hyperfine coupling constant ratios for the latter states in 1-pyrazolyl radical suggest that its ESR spectrum should be conclusive in this concern.

(2) The single-configuration wave function of the two low-lying states $^2A_2$ and $^2B_2$ of both radicals is subject to Hartree–Fock "doublet instability". Due to this phenomenon, asymmetric planar structures (C_s) of lower energy than the symmetric structure (C_{2v}) are obtained at the ROHF level of theory for these states. The present CISD calculations suggest that an appropriate MCSCF treatment of the electron correlation effects should predict a symmetric (C_{2v}) equilibrium geometry.

(3) Although the σ-type doublet state ($^2B_2$) of 1-pyrazolyl radical is predicted to lie about 12 kcal/mol above the lowest π-type doublet ($^2B_1$), at the equilibrium geometry of the former state the latter is calculated to lie about 18 kcal/mol higher in energy. Therefore, on a chemical time scale 1-pyrazolyl can behave as a metastable σ-type radical if it is generated in the excited $^2B_2$ state.

(4) In 1-imidazolyl radical the σ-type doublet ($^2B_2$) is calculated to lie about 29 kcal/mol above the ground state ($^2B_1$). Although at the equilibrium geometry of the former state the latter is predicted to lie only about 6 kcal/mol above, it seems unlikely that if 1-imidazolyl radical is generated in the excited $^2B_2$ state, it would live long enough to behave chemically as a metastable σ-type radical before decaying to the ground state π-type radical.

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cyclo-Dodecaoxygen, O_{12}: Comparison with the Experimentally Characterized S_{12} Molecule

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Abstract: The O_{12} molecule has been examined by using ab initio quantum mechanical methods, specifically self-consistent-field (SCF) theory with basis sets as large as double-ζ plus polarization (DZ+P). The complete molecular structures for O_{12} and the 192-electron system S_{12} have been predicted, along with photoelectron, infrared, and Raman spectra. Comparisons between the two molecules are made throughout. Although O_{12} is predicted to lie energetically above six separated diatomic oxygen molecules, this energy difference is significantly less than suggested by simple bond energy arguments.

Elemental sulfur exists in the solid state as cyclic S_n molecules.[1-3] Although common elemental sulfur is largely S_8 rings, the compound now known to be *cyclo*-S_6 was first prepared[2] in 1891. Moreover, cyclic sulfur compounds as large as S_{20} have been synthesized and characterized.[1-3] Among the larger S_n molecules, the best understood is S_{12}, which was first prepared[4] in 1966. In fact, the stability of S_{12} approaches that of common S_8 rather closely.[5]

The structure of an isolated S_{12} molecule is expected from crystal structures[1-3,6,7] to be of D_{3d} symmetry. The S_{12}·CS_2 complex does indeed display D_{3d} symmetry within the S_{12} moiety, and this experimental structure[6] is shown in Figure 1. Given the stability of S_{12}, a reasonable question is: What about the existence of the valence isoelectronic O_{12} molecule?

In an earlier paper[8] on the smaller O_4 molecule, an extended explanation of the instability of *cyclo*-O_n molecules compared to *cyclo*-S_n molecules was given. To summarize briefly: (a) O–O single bonds are weaker than S–S single bonds, and (b) diatomic O_2 has a larger dissociation energy than diatomic S_2. The conjunction of these two effects means that the process

$$\textit{cyclo}\text{-}S_n(g) \rightarrow \frac{n}{2}S_2(g) \qquad (1)$$

is usually (e.g., for S_6, S_8, and S_{12}) endothermic while that for

$$\textit{cyclo}\text{-}O_n(g) \rightarrow \frac{n}{2}O_2(g) \qquad (2)$$

is predicted to be significantly exothermic.

From an experimental perspective, this analysis[8] means that O_{12} will be much more difficult to prepare in the laboratory than S_{12}. However, if makeable, O_{12} would be a very interesting molecule due to its extremely high energy content. Specifically, for the O_{12} system, the fragmentation reaction (2) is crudely estimated[8] to be 300 kcal/mol exothermic. The goal of the present research is to characterize the unknown molecule O_{12} structurally

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[§] Contribution CCQC No. 48.

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