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An ab Initio Molecular Orbital Study of the Phenyl Radical

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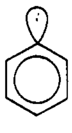
Results of ab initio ROHF and CI calculations on doublet and quartet states of phenyl radical (C_6H_5) are described. In agreement with experiment, the lowest energy state is the σ radical (1^2A_1), which is predicted to have a geometry similar to benzene. The two lowest π radical states (1^2B_1 and 1^2A_2) should have substantially distorted geometries and will be highly polarized. Relative energies (3-21G ROHF) at optimized (STO-3G ROHF) geometries are 1^2A_1 (0.0 eV), 1^2B_1 (2.81), 1^2A_2 (3.77). Addition of polarization functions to C_1 decreases the $^2A_1$–$^2B_1$ gap to 2.68 eV.

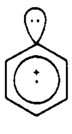
Aryl radicals are believed to be intermediates in a wide variety of thermal and photochemical reactions.[1,2] Many details of their electronic structure, however, are poorly understood. Nearly 20 years ago, Porter and Ward first reported observation of phenyl radicals through flash photolysis of aryl halides,[2a] and assigned the lowest energy optical transition as $^2A_1 \rightarrow {}^2B_1$ (σ radical $\rightarrow$ π radical). Subsequent ESR studies[3] and numerous semiempirical MO calculations[3b,4] have supported a ground-state σ radical, but the involvement of π radicals in phenyl radical chemistry has remained unknown. The potential for distinct σ/π radical chemistry has been strongly suggested through the work of Skell and co-workers on succinimidyl,[5] although this clearly remains a controversial question.[6] In the case of succinimidyl, one of the main objections which might be raised is that molecular orbital calculations predict only a small gap (ca. 1 eV) between σ and π states.[7]

We describe here results of ab initio ROHF and CI calculations on low-lying phenyl radical doublet and quartet states. Optimized geometries are reported for the three lowest doublet states. Our calculations support the possibility that σ and π phenyl radicals are well separated energetically and may exist as discrete, chemically distinguishable species, as has recently been considered by Russell and co-workers.[8] During the course of our work, Pacansky and Brown reported matrix isolation of the phenyl radical and the results of singlet-point SCF calculations on several phenyl radical states.[9] Our computational results are in good qualitative agreement with those reported but further show that the upper doublet states (π radicals) are significantly polarized and will have geometries quite different from the ground-state σ radical.

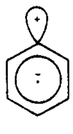
Electronic Structure of the Phenyl Radical. Low-lying electronic states will arise from occupation with five electrons of the in-plane σ, two π, and two π^* MO's, shown in Figure 1. Simple valence-bond descriptions and associated symmetries of the various states are summarized in structures 1–4. Previous molecular orbital calculations have primarily concerned the σ radical **1**.[3,4] The generally excellent agreement with calculated spin densities and other properties[3] and our own calculations on **2**–**4** (vide infra) are entirely consistent with σ radical **1** as the ground state.



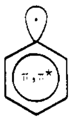
1 (1^2A_1)



2 (1^2B_1, 1^2A_2)



3 (2^2B_1, 2^2A_2)



4 (2^2A_1, 1^2B_2
1^4A_1, 1^4B_2)

In-plane double occupation (**2**) corresponds to two nondegenerate π radical configurations, which result from single occupation of the $1a_2$ or $2b_1$ π MO's. The nondegeneracy of the two resulting states is due to their substantially different electronic distributions and equilibrium geometries (vide infra). This situation is directly analogous to the benzene radical cation or radical anion,[10] or the phenyl cation,[11] and we may expect both 1^2B_1 and 1^2A_2 to exist as stationary points. Promotion (relative to **1**) from $\sigma \rightarrow \pi^*$ yields doublet states (**3**), which we anticipate to be substantially higher in energy than **1** or **2**. Alternatively, in-plane single occupation and $\sigma \rightarrow \pi^*$ excitation (**4**) gives rise to both doublet (one unpaired spin) and quartet states (three unpaired spins). Due to like-state symmetries and the near degeneracy of the pairs of π and π^* MO's, substantial configurational mixing is expected, thus these quartet states are predominantly biconfigurational. This is quite analogous to the π,π^* excited states of benzene.

Computational Methods. All calculations were performed with a modified version of GAMESS.[12] Molecular size precluded the use of large basis sets, thus standard STO-3G and split-valence 3-21G bases[13] were used throughout. A full set of polarization functions ($\alpha = 0.8$) was added to C_1 in the final calculations. Configuration interaction (CI) calculations utilized the graphical unitary group approach (GUGA) of Brooks and Schaefer[14] as implemented in GAMESS. SCF calculations were based on the restricted open-shell Hartree–Fock (ROHF) method of Davidson.[15] ROHF geometry optimizations were per-

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(1) For a review of the various thermal generation methods, see: Nonhebel, D. C.; Walton, J. C. "Free Radical Chemistry"; Cambridge University Press: London, 1974; p 418–466.

(2) Photochemical generation: (a) Porter, G.; Ward, B. *Prog. Roy. Soc. Ser. A* **1965**, *287*, 457. (b) Scaiano, J. C.; Stewart, L. C. *J. Am. Chem. Soc.* **1983**, *105*, 3609 and references therein. (c) Sharma, R. K.; Kharasch, N. *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 36 and references therein.

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(4) For example: (a) Bischof, P. *J. Am. Chem. Soc.* **1976**, *98*, 6844. (b) Arnaud, R.; Subra, R.; Barone, V. *Nouv. J. Chim.* **1982**, *6*, 91. (c) Sakaguchi, K.; Inuzuka, K. *Nippon Kagaku Kaishi* **1976**, 1343.

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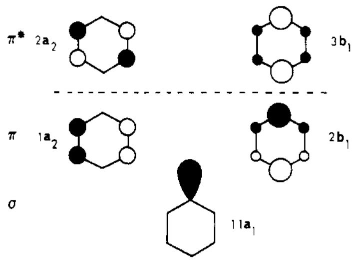
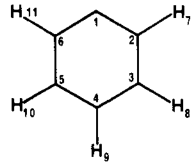


Figure 1. Phenyl radical molecular orbitals.

Table I. Optimized STO-3G ROHF Geometries for Phenyl Radical Doublet States



bond	1^2A_1, Å	1^2B_1, Å	1^2A_2, Å
C_1–C_2	1.378	1.491	1.415
C_2–C_3	1.391	1.345	1.465
C_3–C_4	1.389	1.439	1.383
C_2–H_7	1.080	1.082	1.093
C_3–H_8	1.082	1.084	1.096
C_4–H_9	1.087	1.088	1.077
bond angle	**1^2A_1, deg**	**1^2B_1, deg**	**1^2A_2, deg**
C_2–C_1–C_6	123.70	110.78	107.89
C_1–C_2–C_3	117.66	125.18	127.39
C_2–C_3–C_4	120.44	119.83	120.26
C_3–C_4–C_5	120.08	119.20	116.81
C_1–C_2–H_7	121.73	116.53	118.69
C_2–C_3–H_8	119.56	110.40	120.13

formed by use of an analytical gradient technique, with restriction to C_{2v} symmetry. Use of the pure doublet ROHF wave function avoids contamination with higher spin states, as may occur with UHF calculation.[16]

Configurations for CI were generated from full excitation (up to seven electrons) within the orbital space defined by the in-plane σ MO and the six lowest π MO's. This yields a total of 784 doublet configurations and 392 quartet configurations of all four symmetries (in C_{2v}). The 1^2A_1 eigenvectors were used as a basis for CI.

Results of Calculations: Doublet States. Initial doublet ROHF and CI calculations were performed at the experimental geometry of benzene (minus one hydrogen) with the use of a minimal basis set. This clearly showed the order of doublet states to be $^2A_1 < {}^2B_1 < {}^2A_2$. Geometries for these states were then gradient optimized; results are summarized in Table I. The σ radical geometry (1^2A_1) is quite close to that of benzene and was lowered only 1.5 kcal/mol by optimization. The two upper doublets (π radicals) are predicted and found to be substantially distorted, due to removal of one electron from the π system. This is illustrated in Figure 2, where relative STO-3G ROHF energies are plotted as a function of distortion relative to a benzene-like geometry (all bond lengths = 1.397, angles = 120°). The $^2A_2$ state is stretched along the z axis due to loss of 2,3- and 5,6-π bond order, while the $^2B_1$ state is y axis elongated for similar reasons. At the STO-3G SCF level, the two states do not intersect as geometries are distorted; however, if the $^2A_2$ state were generated, we would expect rapid conversion to $^2B_1$ as a result of nonadiabatic coupling.

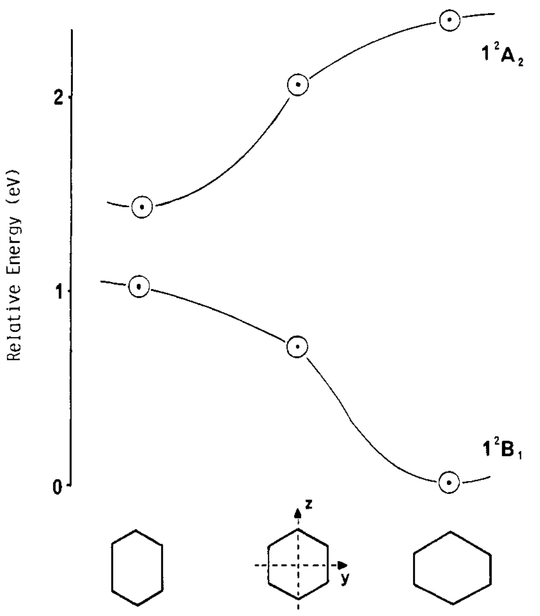


Figure 2. Energies of $^2B_1$ and $^2A_2$ states (STO-3G/ROHF) as a function of geometry.

From doublet CI calculations (vide infra) each of these states is dominated by a single configuration (coefficients 0.942 ($^2A_1$), 0.845 ($^2B_1$), and 0.841 ($^2A_2$). Thus, we expect single configuration ROHF to yield reasonable geometries and energies. MCSCF optimization would provide more accurate results, but this presently is not feasible for such a large molecule.

State energies calculated at various levels are summarized in Table II. Both ROHF and CI calculations clearly demonstrate the $^2A_1 < {}^2B_1 < {}^2A_2$ order. The 3-21G basis set generally provides relative energies comparable to those at the 6-21G or 4-31G levels and significantly better than STO-3G results.[13] Addition of polarization functions at the radical center lowers state energies by ca. 1 eV, with $^2B_1$ deriving somewhat greater relative stabilization than $^2A_1$. It did not prove possible to perform SCF calculations on the 2^2B_1 or 2^2A_2 states (**3**), since these invariably collapsed to lower states; however, CI calculations predict 2^2B_1 (**3**) to be at substantially higher energy. Due to the small CI and use of the $^2A_1$ vectors (which bias results toward this state), we expect the $^2A_1$–$^2B_1$ energy differences to be somewhat exaggerated by CI calculations. Our best estimate for the $^2A_1$–$^2B_1$ gap (3-21g plus pol ROHF) is 2.68 eV, but the true σ radical–π radical gap probably is ca. 2.4 eV.[2a] In solution, the more strongly polarized $^2B_1$ state (vide infra) would be preferentially stabilized, further diminishing the observed gap.

Pacansky and Brown recently reported large (sp) basis set calculations on ground and excited states of phenyl radical, at the geometry of benzene, minus one hydrogen.[9] Relative energies for low-lying states were as follows: 1^2A_1 (0.0 eV), 1^2B_1 (2.93), 1^2A_2 (3.87). Our calculations at SCF optimized geometries for all states yield lower relative energies for the upper states but give the same ordering. A priori, the order of the two lowest doublet excited states could have been reversed by geometry optimization.

Results of Calculations: σ Radical Quartet States. Quartet states ($^4A_1$ and $^4B_2$) result from single occupation of σ, π, and π* MO's with single electrons of like spin. These are directly analogous to benzene triplet states except that there is one additional odd electron. Because these states are biconfigurational, single configuration geometries and SCF are inappropriate, and no geometry optimization was attempted. CI calculations were per-

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[16] For a discussion, see: Pople, J. A. In "Applications of Electronic Structure Theory"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977; Chapter 1, p 1.

Table II. Results of SCF and CI Calculations on Phenyl Radical States[a]

state	dominant configuration	ROHF STO-3G[b]	ROHF[b] 3-21G 3-21G + pol	3-21G CI[c]
1^2A_1	...$(2b_1)^2(1a_2)^2(11a_1)^1$	−227.23435 (0.0)	−228.76839 (0.0) −228.80665 (0.0)	−228.83424 (0.0)
1^2B_1	...$(1a_2)^2(11a_1)^2(2b_1)^1$	−227.12098 (3.09)	−228.66520 (2.81) −228.70799 (2.68)	−228.69321 (3.84)
1^2A_2	...$(2b_1)^2(11a_1)^2(1a_2)^1$	−227.06816 (4.52)	−228.62985 (3.77)	−228.64173 (5.24)
2^2A_1	...$(2b_1)^2(11a_1)^1(1a_2)^1(2a_2)^1$ ...$(1a_2)^2(11a_1)^1(2b_1)^1(3b_1)^1$			−228.67152 (4.43)
1^4A_1	as above			−228.68748 (3.99)
1^2B_2	...$(2b_1)^2(11a_1)^1(1a_2)^1(3b_1)^1$ ...$(1a_2)^2(11a_1)^1(2b_1)^1(2a_2)^1$			−228.64753 (5.08)
1^4B_2	as above			−228.64631 (5.11)
2^2B_1	...$(1a_2)^2(2b_1)^2(3b_1)^1$			−227.56574 (7.31)

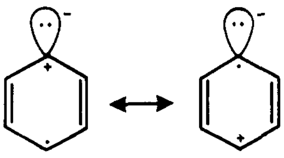
[a] Relative energies (eV) are given in parentheses. [b] At SCF optimized geometries. [c] Full CI among π MO's and in-plane σ orbital at $^2A_1$ geometry.

Table III. Mulliken Populations for Doublet States (3-21G ROHF)

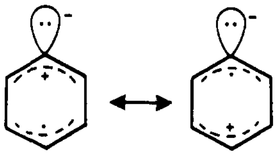
		C_1	C_2	C_3	C_4
1^2A_1	π electrons	0.9473	1.0308	0.9872	1.0168
(σ radical)	all electrons	5.9496	6.2912	6.2291	6.2475
1^2B_1	π electrons	0.3255	0.9264	1.005	0.8109
(π radical)	all electrons	5.9585	6.3194	6.2473	6.1747
1^2A_2	π electrons	0.6375	0.8543	0.7723	1.1094
(π radical)	all electrons	6.0834	6.2805	6.1719	6.2973

formed at the 1^2A_1 geometry with $^2A_1$ vectors. These calculations (Table II) suggest that the lowest quartet state ($^4A_1$) is only slightly higher than $^2B_1$. MCSCF calculations would be necessary to accurately determine the lowest quartet geometry and energy, but it clearly should be less than the 3.99 eV predicted by our calculations.

Charge Distribution in Doublet States. Electronic distributions in σ and π radical states differ appreciably, as shown by their Mulliken populations (Table III). The $^2A_1$ σ radical (3-21G ROHF dipole moment 0.789 D) has balanced σ and π electron distributions, while the $^2B_1$ and $^2A_2$ π radicals (dipole moments 4.21 and 5.13 D, respectively) are strongly polarized. The most dramatic effect occurs at C_1 in $^2B_1$, which has substantial π electron deficiency. The $^2B_1$ π radical is well represented by resonance structure **5a**, while $^2A_2$ is a hybrid of **6a** and **6b**, with the former favored. The π polarization in $^2B_1$ and $^2A_2$ is due to their unbalanced σ population. Thus, excess σ electron density at C_1 results in a π electron deficiency at the same carbon. One might expect this polarization to be enhanced or diminished by para substituents.



5a ($^2B_1$) 5b



6a ($^2A_2$) 6b

Discussion

There are three doublet states potentially involved in phenyl radical chemistry. The ground state ($^2A_1$) is a σ radical, adequately represented by structure 1. There are two low-lying π radical states ($^2B_1 < {}^2A_2$) which are well represented by the resonance structures shown above. A corresponding σ radical quartet state probably is <1 eV above $^2B_1$. For the three doublet states, the order ($^2A_1 < {}^2B_1 < {}^2A_2$) is in good agreement with flash photolysis experiments of Porter and Ward nearly 20 years ago and with more recent SCF calculations by Pacansky and Brown.[9] On the basis of substituent effects on spectra, Porter concluded that the lowest electronic transition in phenyl radical is $^2A_1 \rightarrow {}^2B_1$ (π → n, symmetry allowed).[2a] The observed 0–0 band was at 528.7 nm (2.35 eV). Our results are in complete agreement with this assignment, but our calculated $^2A_1 \rightarrow {}^2B_1$ excitation energy (2.68 eV) is slightly too high.

Numerous matrix ESR studies[3] strongly support a $^2A_1$ ground state. Observed hyperfine couplings of 17.5 (ortho), 6.1 (meta), and 1.9 (para) Gauss are in good qualitative agreement with our atomic spin densities (3-21G ROHF) on hydrogen of 0.00629 (ortho) 0.00172 (meta), and 0.00026 (para).

The ionization potential of phenyl radical has been variously reported to be 8.1, 9.20, or 9.35 eV.[17] On the basis of the $2b_1$ (HOMO) π orbital energy (0.3434 hartree) and Koopman's theorem, we calculate 9.34 eV, in surprisingly good agreement with the latter two values.[18] This is little different from benzene. The predicted ionization potential for the $^2B_1$ state (ionization from $11a_1$) is 8.67 eV. It is possible that both states might be selectively generated in the gas phase.

Finally, we comment on potential chemistry of these two states. The σ ($^2A_1$) phenyl radical is known to be somewhat nucleophilic with relatively low positional and substrate selectivity and presumably low polarity. By contrast, we predict the lowest π radical ($^2B_1$) to be strongly polarized. Its reactivity may well be dominated by what is best described as radical cation character in the π system.

One important question is the potential lifetime of the $^2B_1$ state. Although no spin multiplicity change is required for radiationless decay to $^2A_1$, the relatively large $^2A_1$–$^2B_1$ energy gap (~2.4 eV) and the overlap-forbidden n → π transition suggest a lifetime long enough for observation of characteristic reactivity.

Acknowledgment. I am grateful to Professor Glen A. Russell whose experimental studies of phenyl radical stimulated our own theoretical interest in this species, to Dr. Stephen Elbert for the use of a modified version of GAMESS, and to Professor Harry Svec for a generous allotment of computer time. This work was supported by the National Science Foundation and by Ames Laboratory, USDOE.

Registry No. Phenyl radical, 2396-01-2.

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(18) Koopmans' theorem is of dubious reliability for open-shell species. As pointed out by a referee, the good agreement of observed and calculated first ionization potentials is unexpected. This may be fortuitous; alternatively it may reflect ionization from a closed-shell π orbital rather than the half-occupied σ MO.