Table III. Some Interatomic Distances[a] and Angles[b] in Tetramethylammonium Difumarate

C1–O1	1.203 (3)	C5–O5	1.196 (3)
C1–O2	1.313 (3)	C5–O6	1.318 (3)
C1–C2	1.485 (4)	C5–C6	1.486 (4)
C2–C3	1.298 (4)	C6–C7	1.304 (4)
C3–C4	1.483 (4)	C7–C8	1.486 (4)
C4–O3	1.240 (3)	C8–O7	1.233 (3)
C4–O4	1.279 (4)	C8–O8	1.280 (3)
O1–C1–O2	120.0 (2)	O5–C5–O6	120.6 (3)
O1–C1–C2	123.8 (3)	O5–C5–C6	123.1 (3)
O2–C1–C2	116.1 (2)	O6–C5–C6	116.3 (2)
C1–C2–C3	122.3 (2)	C5–C6–C7	122.0 (2)
C2–C3–C4	124.8 (2)	C6–C7–C8	125.3 (2)
C3–C4–O3	120.3 (2)	C7–C8–O7	119.6 (2)
C3–C4–O4	116.3 (2)	C7–C8–O8	116.1 (2)
O3–C4–O4	123.5 (2)	O7–C8–O8	124.3 (2)
O2–HO2	0.87 (4)	O2···O3	2.600 (3)
O3–HO2	1.73 (4)	O2–HO2–O3	174 (4)
O4–HO4	1.15 (4)	O4···O8	2.450 (3)
O8–HO4	1.30 (4)	O4–HO4–O8	177 (4)
O6–HO6	0.88 (4)	O6···O7	2.584 (3)
O7–HO6	1.71 (4)	O6–HO6–O7	178 (4)

[a] In angstroms. [b] In degrees.

the structure. Thus, the proposal above is confirmed. However, an extended interpretation of the dimaleate and diphthalate spectra must await quantification of the structural effects on chemical shifts in this class of compounds. Interestingly, both the cesium diphthalate[14] and the rubidium diphthalate dihydrate[15] have structures with a hydrogen-bonding scheme very much resemblant of that in the tetramethylammonium difumarate.

Experimental Section

All salts were prepared and analyzed as previously described.[1] The NMR measurements were performed on a Varian XL-200 spectrometer equipped with a probe for CP/MAS (cross-polarization/magic angle spinning) experiments with specimens in the solid state.[16-18] Typically 256 single 0.7-ms cross-polarizations from protons were accumulated with recycle and acquisition times of 2 and 0.1 s, respectively. Spinning rates were 1.9–2.0 kHz. Sideband suppression[9] was applied in all measurements.

X-ray data for tetramethylammonium difumarate were collected on a Huber four-circle diffractometer with monochromated Mo $K\alpha$ (Mo $K\alpha_1$ = 0.709 30 Å) radiation under the control of locally written software.[20] The monoclinic unit cell, space group $P2_1/m$ with a = 6.399 (1) Å, b = 6.776 (2) Å, c = 17.290 (3) Å, and β = 94.22 (2)°, holds two formula units. A hemisphere of reciprocal space was sampled by the $\omega - 2\theta$ scan technique and $\Delta\omega = 0.7° + 0.4° \tan\theta$ to a maximum $(\sin\theta)/\lambda$ = 0.60 Å^{-1}. Three standards measured every 2 h showed no systematic variation. The 2898 reflections were corrected for Lp and absorption effects (μ = 1.1 cm^{-1}). The structure solution was carried out with SHELXS;[21] 1555 reflections with $I > 5\sigma_c(I)$ were used in the refinement with unit weights. Secondary extinction correction[22] gave $q = 3.56\ (7) \times 10^3$. The final structural model with all non-hydrogens anisotropic and hydrogens isotropic (171 parameters) resulted in $R = 0.032$, $R_w = 0.030$, and $S = 0.48$. Some interatomic distances and angles are given in Table III.

Acknowledgment. The nuclear magnetic resonance spectra were taken at the Major Analytical Instruments Facility of the Department of Chemistry, Case Western Reserve University.

Supplementary Material Available: Table of atomic coordinates and thermal parameters and table of anisotropic thermal parameters (2 pages); structure factor table (10 pages). Ordering information is given on any current masthead page.

---

(14) Krol, I. A.; Agre, V. M.; Trunov, V. K.; Avdonina, L. M. *Koord. Khim.* **1983**, *9*, 687; Cambridge Structural Database, ref code: CAHLUS.

(15) Küppers, H. *Z. Kristallogr.* **1977**, *146*, 269.

(16) Schaefter, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1975**, *8*, 291.

(17) Pines, A.; Gibby, M. G.; Waugh, J. S. *Chem. Phys. Lett.* **1972**, *15*, 373.

(18) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201 and references cited therein.

(19) Dixon, W. T. *J. Magn. Reson.* **1981**, *44*, 220.

(20) Svensson, C. *Acta Crystallogr.* **1987**, *A43*, C270.

(21) Sheldrick, G. M. In *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University: Oxford, 1985; pp 175–189.

(22) Becker, P. J.; Coppens, P. *Acta Crystallogr.* **1974**, *A30*, 129.

An AM1 Theoretical Study of the Structure and Electronic Properties of Porphyrin

Charles H. Reynolds

Computer Applications Research, Rohm and Haas Company, Spring House, Pennsylvania 19477

Received June 20, 1988

AM1 calculations are reported for the parent free base porphyrin. These calculations show that the predicted structure for this molecule is qualitatively different depending on the type of wave function employed. A RHF wave function leads to a relatively low-symmetry bond-alternating structure for porphyrin whereas a UHF wave function leads to the expected D_{2h} nearly bond-equivalent structure. The UHF energy is on the order of 1 eV lower than the RHF energy, a condition that is normally found only for biradicals. These results are interpreted in terms of electron-pair correlation effects and a π system for porphyrin isoelectronic with 18-annulene.

Introduction

The structure and electronic properties of porphyrin have been subjects of considerable interest for many years,[1] due to the importance of this molecule as the simplest example of a class of biologically significant ligands. Numerous X-ray[2,3] and NMR[4] studies of variously substituted porphyrins have been reported in the literature, and they all indicate a highly symmetric structure for porphyrin with nearly equivalent C–C bonds. Theoretical studies have also been undertaken,[5-17] but because of the large size

---

(1) *The Porphyrins*; Dolphin, D., Ed.; Academic: New York, 1979.

(2) Chen, B. M. L.; Tulinsky, A. *J. Am. Chem. Soc.* **1972**, *94*, 4144.

(3) Webb, L. E.; Fleischer, E. B. *J. Chem. Phys.* **1965**, *43*, 3100.

(4) Frydman, L.; Olivieri, A. C.; Diaz, L. E.; Frydman, F. G. M.; Mayne, C. L.; Grant, D. M.; Adler, A. D. *J. Am. Chem. Soc.* **1988**, *110*, 336 and references therein.

(5) Merz, K. M.; Reynolds, C. H. *J. Chem. Soc., Chem. Commun.* **1988**, 90.

0022-3263/88/1953-6061$01.50/0

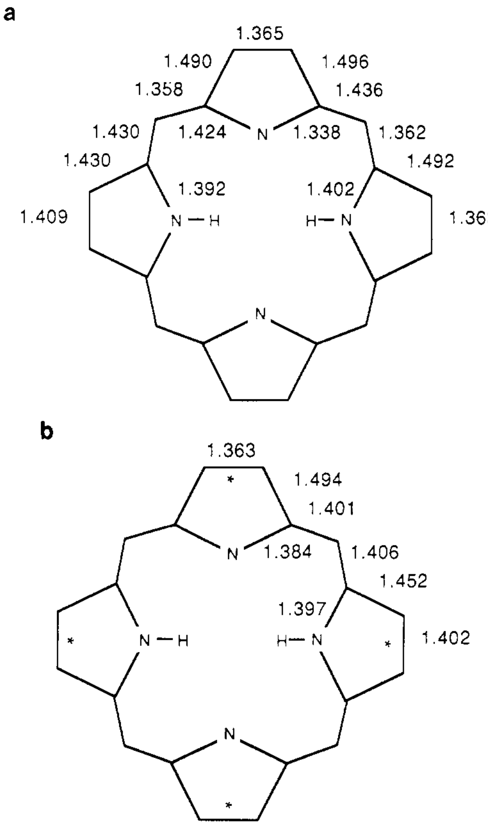

Figure 1. Calculated bond lengths (angstroms) for porphyrin using the (a) AM1 and (b) UAM1 methods. Molecular symmetries are C_{2v} and D_{2h}, respectively.

of porphyrin, most of these studies have had to resort to imposing severe restrictions on the geometry or have simply forgone any optimization whatsoever. Such restrictions are necessarily fraught with peril, particularly if points of extrema are not characterized by calculating force constants. Results are reported here for complete geometry optimization of porphyrin by using the semiempirical AM1[18] method. AM1 has been chosen because, like its predecessor MNDO,[19] it has been extensively tested, and has been found to reproduce the ground-state properties of organic molecules very well. In addition, AM1 is computationally efficient and therefore allows for thorough geometry optimization of porphyrin.

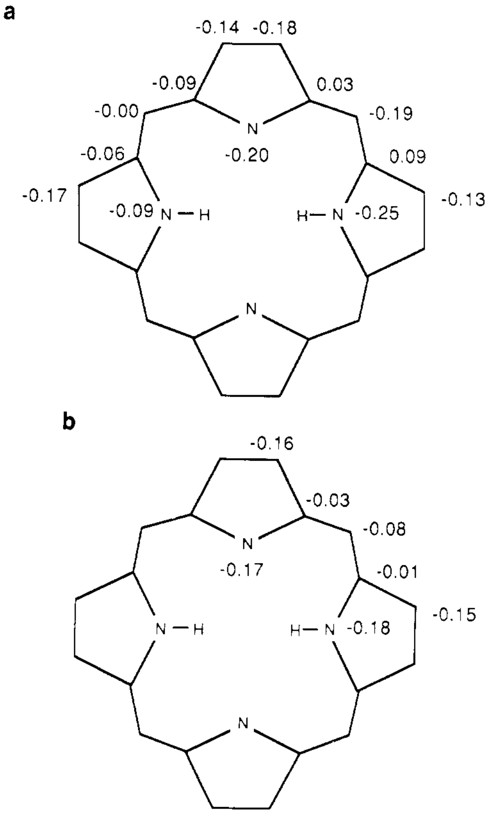

Figure 2. Calculated (a) AM1 and (b) UAM1 partial charges for porphyrin.

Table I. AM1 Calculated Heats of Formation (kcal/mol) for Porphyrin

method	ΔH_f	E_{rel}	classification
RHF	242.8	21.2	minimum
UHF	221.6	0	minimum
RHF (D_{2h})	249.5	27.9	transition state
CI (D_{2h})	232.7	11.1	

Computational Details

The MOLY[20] molecular graphics/modeling package was used to display and preoptimize the structures in this study. All geometries were completely optimized without making any assumptions by using the AM1 and spin unrestricted, UAM1,[21] Hamiltonians, as implemented in the AMPAC[22] computer program. All stationary points were characterized by calculating force constants.[23]

Results and Discussion

The AM1 calculated energy, geometry and atomic charges are reported in Table I and Figures 1 and 2, respectively. The geometry and charges are surprising since neither exhibits anything approaching the expected D_{2h} symmetry. The geometry seems most consistent with a localized bond-alternating structure, except for one pyrrole ring that is aromatic. This is completely inconsistent with the bond-equalized D_{2h} crystal structure determined by Chen and Tulinsky.[2]

It has been found previously[24-26] that some conjugated polyenes, such as 18-annulene, require a UHF or CI wave

---

(6) Nagashima, U.; Takada, T.; Ohno, K. *J. Chem. Phys.* **1986**, *85*, 4524.

(7) Pinchunk, V. M.; Koroskii, V. A.; Lobanov, V. V. *Teor. Eksp. Khim.* **1984**, *20*, 206.

(8) Bersuker, G. I.; Polinger, V. Z. *Chem. Phys.* **1984**, *86*, 57.

(9) Sarai, A. *J. Chem. Phys.* **1984**, *80*, 5341.

(10) Rawlings, D. C.; Davidson, E. R.; Gouterman, M. *Theor. Chim. Act* **1982**, *61*, 227.

(11) Sarai, A. *J. Chem. Phys.* **1982**, *76*, 5554.

(12) Sarai, A. *Chem. Phys. Lett.* **1981**, *83*, 50.

(13) Kuzmitsky, V. A.; Solovyov, K. N. *J. Mol. Struct.* **1980**, *65*, 219.

(14) Sambe, H.; Felton, R. H. *Chem. Phys. Lett.* **1978**, *61*, 69.

(15) Petke, J. D.; Maggiora, G. M.; Shipman, L. L.; Christoffersen, R. E. *J. Mol. Spectrosc.* **1978**, *71*, 64.

(16) Chantrell, S. J.; McAuliffe, C. A.; Munn, R. W.; Pratt, A. C. *Coord. Chem. Rev.* **1975**, *16*, 259, and references therein.

(17) Almlöf, J. *Int. J. Quantum Chem.* **1974**, *8*, 915.

(18) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(19) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899 and 4907.

(20) Bright, M. A.; Dyott, T. M.; Fujimoto, T. T.; Pierce, T. H.; Reynolds, C. H.; Stuper, A. J.; Zander, G. S. *QCPE Bull.* **1987**, *7*, 86.

(21) Pople, J. A.; Nesbet, R. K. *J. Chem. Phys.* **1954**, *22*, 571.

(22) Dewar, M. J. S.; Stewart, J. J. P. *QCPE Bull.* **1986**, *6*, 24.

(23) McIver, J. W.; Komornicki, A. *Chem. Phys. Lett.* **1971**, *10*, 303. McIver, J. W.; Kormornicki, A. *J. Am. Chem. Soc.* **1972**, *94*, 2625.

(24) Jug, K.; Fasold, E. *J. Am. Chem. Soc.* **1987**, *109*, 2263 and references therein.

(25) Dewar, M. J. S.; McKee, M. L. *Pure Appl. Chem.* **1980**, *52*, 1431.

(26) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* **1985**, *107*, 289.

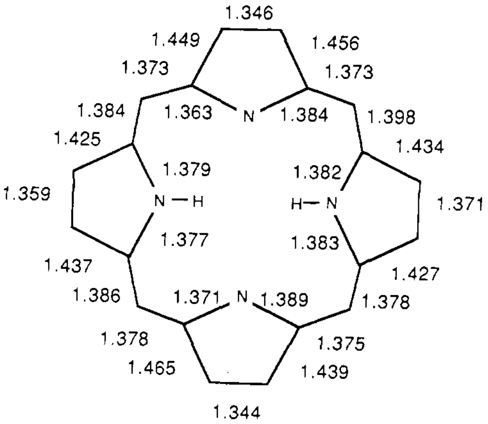

Figure 3. Bond lengths from the crystal[2] structure of porphyrin.

function for accurate description of their molecular properties. This is sometimes referred to as the singlet instability problem and has been described elsewhere.[27] Given this knowledge and the odd properties calculated by the RHF method, porphyrin was recomputed with the spin unrestricted, UAM1, treatment. The RHF and UHF energies for porphyrin differ significantly, with the UHF energy being on the order of 1 eV more stable. This is a large difference since normally the RHF and UHF energies are virtually identical for ground-state singlets, the only usual exception being biradicals.

For biradicals, the RHF wave function gives energies that are much too positive because the two uncoupled electrons are forced to share a single molecular orbital. The UHF wave function removes this restriction by explicitly splitting the α and β electrons into separate MO's and leads to a significantly more negative electronic energy. Thus, a 1 eV or greater difference in the RHF and UHF computed energies, a condition met by porphyrin, is often taken as direct evidence for a biradical.[28] Since porphyrin is not expected to be a biradical, the observed large RHF–UHF energy gap would be surprising if it were not for the previously mentioned precedence for this type of behavior in conjugated polyenes. In the case of 18-annulene, semiempirical[24,25] calculations show that the RHF and UHF energies differ markedly, with the UHF results being much more negative. This result has been interpreted by Dewar and McKee[25] in terms of the greater electron-pair correlation found in symmetric conjugated polyenes, an explanation also supported by ab initio calculations.[26] It seems that, as is the case with biradicals, the π MO's in porphyrin and 18-annulene are near enough to degeneracy so that promotion of an electron from HOMO to LUMO is more than compensated energetically by the resultant reduction in electron–electron repulsion. This requires allowance for electron correlation beyond that normally absorbed in the AM1 parameters. One way of allowing for this extra correlation is to separate the α and β spin electrons into independent spatial orbitals, i.e. a UHF wave function.

The UAM1 computed geometries are also of considerable interest. While the RHF geometry (Figure 1a) exhibits strong bond alternation and appears to be best represented as a single classical Kekule structure, the bond lengths (Figure 1b) calculated by the unrestricted method are much more nearly equivalent. Further, the overall UAM1 geometry exhibits a much higher degree of symmetry (D_{2h} instead of C_{2v}), consistent with the crystal structure.[2] The UAM1 and experimental geometries compare well (Figure 3) although the UHF calculated bond lengths are on average 0.025 Å longer than those found in the crystal study. Much of this error occurs because even the UHF calculated bond lengths show a greater degree of bond alternation than those of the X-ray structure. Nevertheless, the significant structural trends are reproduced by the UHF results. For example, comparison of the UAM1 amino and imino nitrogen–carbon bonds with the X-ray structure shows that in both cases the imino bonds are shorter. The calculated bond lengths are between 0.008 and 0.017 Å longer than the crystal structure, but the trends are the same. Likewise, the peripheral C–C bonds opposite the imino nitrogens (starred) are calculated and measured to be shorter than the peripheral C–C bonds opposite the amino nitrogens (also starred). Once again, however, the calculated bond distances are systematically longer, this time by approximately 0.017 Å. The UAM1 geometry is planar (indeed planarity can be enforced without any cost in energy) as is the experimental geometry. Even so, it is interesting to note that the porphyrin ring is a good deal more flexible than might be imagined. This is clear from the small calculated vibrational frequencies for distortion out of the plane and from calculations where the molecule was intentionally twisted away from planarity.

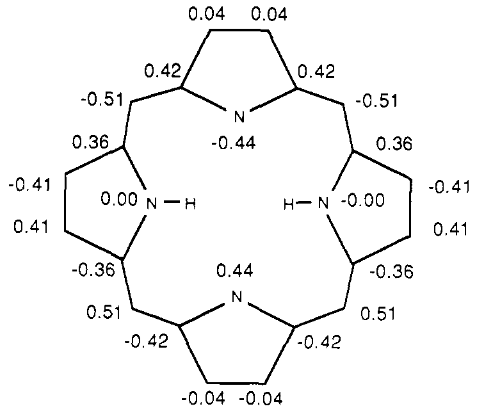

Figure 4. UAM1 calculated π spin densities for porphyrin.

As is the case for the energies, the large difference between RHF and UHF computed geometries finds analogy in 18-annulene. The restricted and unrestricted geometries calculated for 18-annulene differ qualitatively,[24-26] with the restricted treatment favoring a bond alternating D_{3h} structure and the UHF or CI treatments favoring a more symmetric D_{6h} structure. This has been observed with both semiempirical[24,25] and ab initio[26] methods. So in addition to increasing stability, electron correlation also has the effect of equalizing the bond lengths in large cyclic polyenes, which leads to a subsequent increase in their overall symmetry. This shift away from bond alternation upon moving to a UHF or CI wave function is due to spatial uncoupling of the π electrons, which favors delocalization. Further, the qualitative difference in molecular symmetry found upon moving from a RHF to UHF wave function is not limited to the geometry, but apparently extends to all computed molecular properties for porphyrin. So, while the AM1 partial charges (Figure 2a) are not consistent with D_{2h} symmetry, the UAM1 (Figure 2b) charges are.

The UAM1 π spin densities for porphyrin are reported in Figure 4. Scrutiny of the calculated spin densities indicates: (1) that the α and β orbitals have significantly different spatial distributions, and (2) that one pair of nitrogens and four of the peripheral carbons bear none of

---

[27] Cizek, J.; Paldus, J. *J. Chem. Phys.* **1967**, *47*, 3976.

[28] Dewar, M. J. S.; Ford, G. P.; Reynolds, C. H. *J. Am. Chem. Soc.* **1983**, *105*, 316 and references therein.

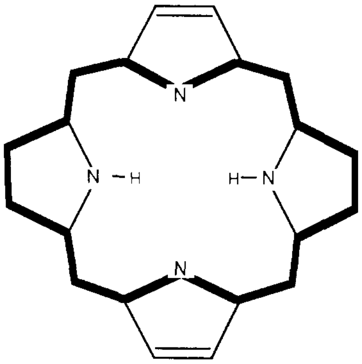

Figure 5. The 18-annulene backbone superimposed on porphyrin.

the unpaired spin. Similarly, while most of the UHF carbon–carbon bonds are more or less intermediate between single and double, two are not. These bonds join the four peripheral carbons which, as pointed out above, bear no spin density. The preceding observations lead one to conclude that two of the peripheral double bonds and the two amino nitrogens are more or less isolated electronically from the rest of the porphyrin π system. Removing these "isolated" atoms effectively leaves behind an 18-annulene π system (Figure 5) and may explain some of the similarities already noted between the geometric and electronic properties of porphyrin and 18-annulene. Indeed, it appears that all of the calculated properties for porphyrin can be rationalized in terms of one monocyclic conjugated π system, isoelectronic with 18-annulene, connected to two essentially isolated double bonds and two equally isolated amino nitrogens. This is not the first time such a representation has been proposed,[29-31] but this is the first theoretical evidence in support of such a representation.

This picture of the electronic structure of porphyrin has some interesting implications. First, it means that two of the double bonds should be chemically distinct from the rest of the π system. For example, oxidation or reduction of porphyrin should not involve the amino nitrogens or the two peripheral double bonds opposite the imino nitrogens. Second, this interpretation removes the objection[32] raised in applying the Hückel $4n + 2$ rule to porphyrin, that Hückel's rule is valid only for monocyclic π systems.[33] For all practical purposes the π system in porphyrin is monocyclic. Therefore, porphyrin can formally be regarded as possessing an 18-electron aromatic ring, although it is debatable how much stability aromaticity imparts to a ring of this size. It should be pointed out that the shift in molecular properties obtained by using UHF or CI wave functions for large conjugated systems, such as porphyrin, has nothing to do with aromaticity. It is simply a consequence of the near degeneracy of the HOMO and LUMO, which occurs in these systems. Bond equalization, energy reduction, and an increase in molecular symmetry are all consequences of electron correlation predominating over the HOMO–LUMO excitation energy. As such, the same trends should be exhibited by acyclic polyenes as well.

Finally, the AM1 energy for porphyrin where D_{2h} symmetry has been externally imposed is reported in Table I. As expected, the D_{2h} energy is higher than the less symmetric structure by 6.7 kcal/mol. In addition, the calculated force constants demonstrate that the RHF D_{2h} structure is *not a minimum* on the potential surface as has often been assumed but is instead the transition state for interconversion of localized-bond Kekule structures. Inclusion of 4 × 4 CI reduces the energy of the D_{2h} structure by approximately 17 kcal/mol (Table I) and leads to atomic charges which show the proper symmetry. Unfortunately, it proved impossible to reduce the gradients sufficiently to calculate reliable force constants for this structure, so whether it is a minimum remains in doubt. The CI results do, however, bear further witness to the unusual electronic structure of porphyrin and the need to go beyond the RHF method to achieve even qualitative agreement with experiment.

Conclusion

The RHF calculated structure for porphyrin exhibits strong bond alternation leading to overall C_{2v} symmetry. UHF calculations lead to significant energy lowering and increase the molecular symmetry to the expected D_{2h}. These results indicate that porphyrin is not a simple closed-shell molecule, but instead has an electronic structure in which the π electrons are significantly decoupled. This is consistent with previous ab initio and semiempirical studies of another large conjugated polyene, 18-annulene. In fact, porphyrin seems best represented as an 18-annulene analogue in which two double bonds and two nitrogens are isolated electronically from the 18-electron monocyclic π system.

Registry No. Porphyrin, 101-60-0.

---

(29) Clezy, P. S.; Fookes, J. R.; Sternhell, S. *Aust. J. Chem.* **1978**, *31*, 639.

(30) Silvers, S. J.; Tulinsky, A. *J. Am. Chem. Soc.* **1967**, *89*, 3331.

(31) Crossley, M. J.; Harding, M. M.; Sternhell, S. *J. Org. Chem.* **1988**, *53*, 1132.

(32) Dewar, M. J. S.; Healy, E. F.; Ruiz, J. *Pure Appl. Chem.* **1986**, *58*, 67.

(33) Dewar, M. J. S.; Dougherty, R. C. *The PMO Theory of Organic Chemistry*; Plenum: New York, 1975.