tivation energy for inward rotation of the hydroxy group is 5.8 kcal/mol above that of the parent system. That of the hydroxy outward transition structure is 4.8 kcal/mol lower than the parent structure.

Model transition structure calculations have also been performed on both modes of opening of 3-*tert*-butyl-3-hydroxycyclobutene. In both cases, the *tert*-butyl group is placed in the position of the methyl group in the transition structures discussed above. The *tert*-butyl conformation is fully staggered and was given the CC and CH bond lengths and CCH bond angles of the STO-3G-optimized neopentane.[12] The calculations indicate that the *tert*-butyl group prefers to rotate inward, even though it is extremely large. The activation energy at the 3-21G level of the hydroxy-in, *tert*-butyl-out transition structure, 14, is 4.0 kcal/mol higher than that of the hydroxy-out, *tert*-butyl-in transition structure, 15. Since the hydroxy

14   15
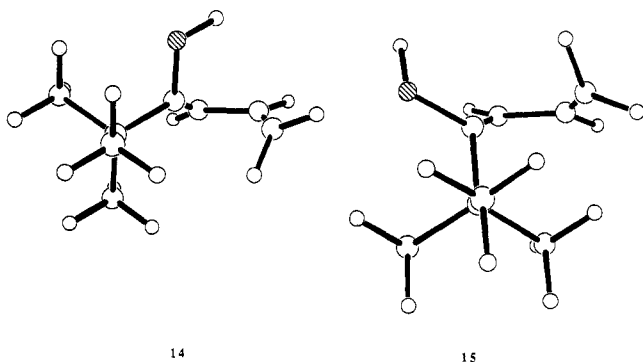
outward preference is 16 kcal/mol, the inherent preference for *tert*-butyl to rotate outward must be approximately 12 kcal/mol, although Curry and Steven have shown that this value is more nearly 7 or 8 kcal/mol.[9] In spite of this incredible steric effect, the *tert*-butyl is predicted and found to rotate inward due to the electronic effect of the small hydroxy group.

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A Conformational Criterion for Aromaticity and Antiaromaticity

Summary: A conformational criterion for aromaticity and antiaromaticity is suggested: relative to planar reference geometries, folding of aromatic and antiaromatic systems results in large endothermic and exothermic changes, respectively. A series of 8π-electron heterocyclic systems were found to be highly flexible and are therefore classified as nonaromatic rather than antiaromatic.

Sir: The concept of aromaticity has evolved dramatically over the last two centuries into a cornerstone for modern theories of chemical structure and reactivity.[1–3] In particular, the π-electron analysis originated by Huckel[4] allows predictions of physical and chemical behavior of cyclic conjugated systems. The extension of Huckel's work by Frost[5] and by Breslow[6] led to the $(4n + 2)\pi$-electron criterion for aromaticity and the $4n\pi$-electron criterion for antiaromaticity, which are so widely accepted that they have achieved the level of dogma in modern organic chemistry. However, there are classes of compounds whose properties are not correctly predicted by using these criteria, and there remains a need for an unambiguous operational definition of aromaticity and antiaromaticity.[7] We report here the preliminary details of a novel computational approach that allows direct evaluation of aromaticity and antiaromaticity.

Inherent in all definitions of aromaticity and antiaromaticity is the notion that a planar ring system maximizes overlap of the atomic p orbitals contributing to the π-system. This π-interaction is highly stabilizing for aromatic systems but destabilizing for antiaromatic systems. Deviations from planarity of the molecular framework will disrupt the π-overlap and consequently affect the energy. Therefore probing the potential energy hypersurface for various geometries should permit determination of the aromatic or antiaromatic nature of a species. We have carried out an ab initio (Hartree–Fock) molecular orbital study[8] of a series of potentially antiaromatic 8π-electron, six-membered ring systems (1–6), of
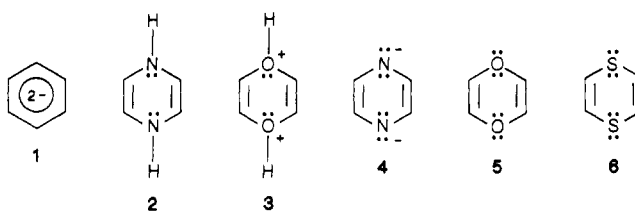
which the singlet benzene dianion, $C_6H_6^{2-}$ (1), is the prototype. Energies were calculated for a series of geometries with varying distortions from planarity (see Table I). For a series of folding angles (the 2–1–4–5 dihedral angle),[9]

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Table I. Calculated 6-21G Folding Energies[a]

	folding angle,[b] deg	energy, hartrees	rel energy, kcal/mol
1	180.0[c]	-229.96210	16.4
	180.0[d]	-229.98651	0.0
	170.0	-230.02041	-20.2
	160.0	-230.02041	-20.2
	166.9[e]	-230.02048	-20.2
2	180.0[d]	-263.47526	0.0
	170.0	-263.47990	-2.9
	160.0	-263.47873	-2.2
	172.2[e]	-263.47994	-2.9
3	180.0[d]	-303.47626	0.0
	170.0	-303.47684	-0.4
	160.0	-303.47793	-1.0
	151.7[e]	-303.47844	-1.4
4	180.0[d]	-261.96375	0.0
	170.0	-261.96375	0.0
	160.0	-261.96352	0.1
	179.6[e]	-261.96375	0.0
5	180.0[d]	-303.05129	0.0
	170.0	-303.05909	0.2
	160.0	-303.05000	0.8
	179.9[e]	-303.05129	0.0
6	180.0[d]	-948.51254	0.0
	170.0	-948.51292	-0.2
	160.0	-948.51397	-0.9
	134.0[e]	-948.51678	-2.7

[a] 3-21G folding energies show the same behavior. [b] C_{2h} symmetry was imposed for nonplanar geometries; planar reference geometries were restricted to D_{2h} or D_{6h}, respectively. [c] D_{6h} symmetry was imposed. [d] D_{2h} symmetry was imposed. [e] The folding angle was optimized.

complete geometry optimizations were carried out within the symmetry constraints specified in the table. The minimum-energy conformations are nonplanar in four of the six cases, (1, 2, 3, and 6), as might be expected for potentially antiaromatic systems (and in accord with other experimental and computational studies[10-12]). Two anomalies were observed, however. First, the minimum-energy structures of pyrazine dianion (4) and dioxin (5) are planar (a structural feature previously suggested for 5 on the basis of experimental data[13,14] and computations at lower levels of theory[15,16]). Second, the energies required to force 2, 3, and 6 into planar geometries are all less than 3 kcal/mol; each exhibits a high degree of conformational flexibility. The optimum (planar vs nonplanar) geometries of 2 and 3 are reversed by removal of two hydrogens for which orbital interactions are nominally orthogonal to the π system. The nonplanarity of 6 (6-21G calculations) has previously been ascribed to angle strain in the σ framework.[17] Only benzene dianion exhibits the behavior anticipated for an antiaromatic species: a nonplanar minimum-energy conformation and a large energy required to attain planarity. Clearly (and in contrast to previous suggestions by us[18] and others[19-21]) a nonplanar

minimum-energy conformation is by itself insufficient to classify a system as antiaromatic.

We have previously reported the folding energies for 6π-electron aromatic compounds 8 and 9,[18] and we have
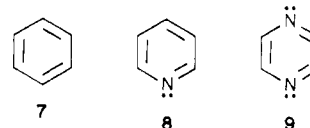
now carried out the corresponding calculations with the archetypical aromatic compound, benzene (7). Folding to 160° requires 15, 9, and 8 kcal/mol, respectively, for 7, 8, and 9. All three $(4n + 2)\pi$-electron species exhibit conformational rigidity, in marked contrast to the flexibility of 2-6. Moreover, the computed energy for distorting 7 from planarity is greater than that for either 8 or 9, which are generally accepted to have a smaller degree of aromaticity than benzene. On this basis, we propose that our folding calculations afford a novel method for assessing aromatic and antiaromatic character: *the conformational criterion for aromaticity and antiaromaticity.* Relative to planar reference geometries of maximum symmetry, folding of aromatic and antiaromatic systems results in large endothermic and exothermic changes, respectively. Aromatic compounds are planar and strongly resistant to folding, whereas antiaromatic systems exhibit large energy decreases when permitted to relax (fold) from planar geometries to nonplanar, minimum-energy conformations. According to this criterion, systems 2, 3, and 6, which have shallow folding energy curves, are *nonaromatic*. As a corollary to this criterion, antiaromatic systems could also exhibit exothermic changes by distorting from maximum symmetry while remaining planar. This could be of particular importance in smaller ring systems as nonplanar distortions of the σ framework become unfavorable. For example, distortion from D_{4h} to D_{2h} symmetry is found for the optimum structure of cyclobutadiene.[22,23] Even in the case of six-membered rings this effect can be seen for the benzene dianion (1, which can relax from the unfavorable D_{6h} geometry either by folding or (to a smaller extent) by in-plane distortion to D_{2h} symmetry.

To the extent that σ and π effects are independent,[23] the energy change that results from folding must be directly related to the resonance energy of the planar system. We have compared the folding energies of compounds 1, 5, and 7 to their respective Dewar Resonance Energies (DRE's),[24] which were calculated as described by Dewar[25] except at the ab initio 6-21G level.[26] Our classifications of 7, as aromatic, 1, as antiaromatic, and 5, as nonaromatic, are in agreement with the Dewar formalism, which leads to DRE values of 18, -62, and -5 kcal/mol, respectively. Our ab initio DRE for benzene agrees well with Dewar's previously reported value of 20 kcal/mol.[27]

The conformational criterion for aromaticity and antiaromaticity offers several advantages over currently

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available criteria. First, it avoids the need for an arbitrary or hypothetical external reference structure; instead, we employ the planar geometry of the actual system being studied as an internal reference. Second, our computational approach enables us to consider systems that are experimentally inaccessible, providing a means to evaluate the degree of aromaticity or antiaromaticity of experimentally unobservable species. Third, the computations can provide a quantitative measure of the degree of aromaticity or antiaromaticity. Work aimed at broadening the scope and applicability of this method is currently underway in our laboratory.

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Nickel-Catalyzed Silylolefination of Dithioacetals. A Stereoselective Way to Vinylsilanes[1]

Summary: (*E*)-Vinylsilanes are synthesized stereoselectively in good yields from dithioacetals and Me$_3$SiCH$_2$MgCl in the presence of a catalytic amount of NiCl$_2$(PPh$_3$)$_2$.

Sir: Vinylsilanes demonstrate an enormous variety of fascinating applications in organic synthesis.[2,3] A number of procedures have been available for their preparations and most of them use alkynes as starting materials.[4] It is noted that the reaction of (silylmethyl)magnesium halide reagent with carbonyl compounds affords exclusively the corresponding desilylated olefins.[5] Some modified silyl reagents have been employed for the synthesis of vinylsilanes;[6] none of them, however, are easily accessible. The transition-metal-catalyzed coupling reaction of aryl or vinyl thioethers with Grignard reagents is well-documented.[7]

Recently we found that benzophenone dithioacetal can couple with Grignard reagents in the presence of a nickel catalyst to give the alkylated olefin (eq 1).[8] We felt that
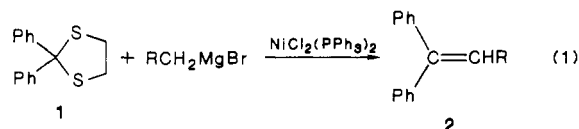
this reaction could be exploited in the synthesis of vinylsilanes. As part of our continuing interest in the transition-metal-mediated C–S bond cleavage reactions[8-10] and, in particular, the synthetic applications of dithioacetals,[8,10] we present here a convenient method for the stereoselective synthesis of vinylsilanes (eq 2).
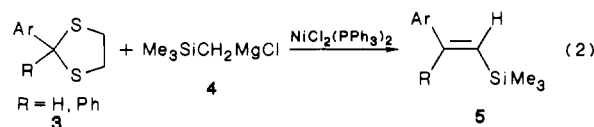
In a typical procedure, a mixture of dithioacetal, 3 equiv of Me$_3$SiCH$_2$MgCl (4), and 5 mol % of NiCl$_2$(PPh$_3$)$_2$ in ether–benzene or ether–THF was heated under reflux overnight. After the usual workup, the corresponding vinylsilane was obtained. The results are tabulated in Table 1.[11]

As can be seen from Table I, a variety of (*E*)-vinylsilanes were synthesized in good yields. The presence of electron-donating substituents (entries 2-5) has no effect on the yields of the reactions. It is particularly noteworthy that the ethereal linkages in **3d** and **3e** are stable under the reaction conditions.[12] Substrates containing two dithioacetal functions behaved similarly. Thus, both *o*- and *p*-phthalaldehyde dithioacetals (**3f**, **3g**) afforded the bis-silylolefination products in satisfactory yields (entries 6 and 7).

Aryl halides are known to couple with the Grignard reagent in the presence of a nickel catalyst.[13] Accordingly,

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