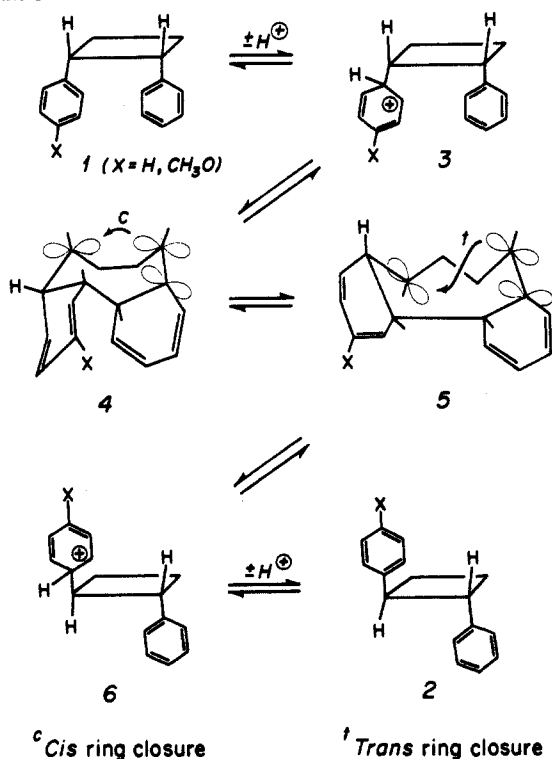


Scheme I



ment to a cyclooctenyl carbenium ion, **4**. Reclosure of the cyclobutyl ring directly from **4** would regenerate the protonated cis diastereomer **3**; however, **4** may alternatively suffer a conformational change to give **5**. Unlike **4**, which is certainly constrained to reclose with cis geometry, conformer **5** may undergo trans ring closure to afford **6** and, ultimately, **2**. The fact that no cis diastereomer could be detected in reaction mixtures which were allowed to approach equilibrium apparently reflects a large (≥ 3 kcal/mol)¹² free energy difference between the cis and trans diastereomers of the 1,2-diarylcyclobutanes in this study.

In contrast to the analogous reaction of *cis*-1,2-diarylcyclopropanes, the rates of stereomutation of *cis*-1,2-diarylcyclobutanes **1a** and **1b** are slower than the rates of deuterium exchange on their aryl rings. This fact may be the consequence of a relatively high barrier to (1) the rearrangement of **3** to **4**, (2) the interconversion of ion conformers **4** and **5**, or (3) both of these steps. Ongoing studies in our laboratory are aimed at resolving these questions and further defining the nature and scope of this unusual reaction type.

In conclusion, the present observations constitute the first evidence of a *general*, proton-catalyzed *cis*-*trans* stereomutation reaction in 1,2-diarylcycloalkanes.

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(11) Note that we depict ipso protonation in this scheme even though the isotope incorporation results do not require it. Our examination of appropriate molecular models suggested to us that the interconversion of the homoallylic carbenium ions **4** and **5**, as well as **5** and **6**, would be facilitated by tetrahedral geometry at C-1'; conversely, these interconversions appear to be relatively difficult in molecular models if C-1' is sp^2 hybridized. Therefore, we currently disfavor a plausible, alternative scheme initiated by protonation at C-3'. The fact that no deuterium was incorporated into the unsubstituted ring when *cis*-1-(4-methoxyphenyl)-2-phenylcyclobutane was allowed to react in TFA-*d* precludes another alternative mechanism in which protonation of the unactivated ring is followed by ring-opening to a benzylic carbenium ion that could reclose to give *trans* cyclobutane.

(12) Our HPLC detection limits for the **1a,b** system were $\sim 200:1$ (Zorbax C-8 reverse-phase column, 4:1 methanol-water, refractive index detection).

Radical Anions. Electron Affinities of Benzene, Naphthalene, and Anthracene Having the Substituents CHO, CN, and NO₂

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We have recently reported determinations¹⁻⁷ of electron affinities based on measurement of gas-phase electron-transfer equilibria (1). These lead to ΔG_1° values. Determination of the



equilibrium constants K_1 at different temperatures lead to ΔH_1° and ΔS_1° . Generally ΔS_1° is small such that $\Delta G_1^\circ \approx \Delta H_1^\circ$ within less than 1 kcal/mol. By anchoring a ΔH_1° scale from connected equilibria to a few compounds (SO₂, NO₂ with known absolute EA values, one obtains the absolute EA for all compounds in the scale. Determinations of EA's for close to 100 compounds were obtained in this manner.¹⁻⁸

Here we consider the electron affinities of a selected group of benzenes,^{1,5,6,9} naphthalenes,^{6,9} and anthracenes,⁷ namely, those carrying the strong-electron-withdrawing substituents X = CHO, CN, and NO₂. The changes of substituent effects with increasing size of the aromatic system observed for these compounds are quite interesting. The electron affinities are shown in Figure 1 plotted vs. the Hammett $\sigma_p^-(g)$ parameter (see Table IV of ref 10) on the basis of the substituent effect on the gas-phase acidities of phenols.^{10,11} Also shown in Figure 1 are the electron affinities of the 1,4 doubly substituted benzenes^{1,5} X-C₆H₄NO₂ and X-C₆H₄CN and the relative gas-phase acidities¹⁰ of the 1,4-phenols X-C₆H₄OH. The following trends are observed. The increase of the electron affinity due to the electron-withdrawing substituent X; i.e., the slope ρ in Figure 1 decreases in the series benzene, naphthalene, anthracene. Similarly, the ρ values decrease from X-C₆H₅ to X-C₆H₄CN to X-C₆H₄NO₂. Thus the approximate overall trend observed is that the ρ value decreases as the electron affinity of the first member (X = H) in a given series increases. This effect is not surprising, the increasing electron affinities of the first members X = H corresponds to progressively lower electron density in the π^* -type singly occupied molecular orbital (SOMO) extending over the aromatic ring of the negative ion. Thus, in the higher electron affinity compounds the electron-withdrawing X, attached to a ring carbon, has less SOMO electron density to operate on.

In addition to the above effect, there is an interesting reversal of the substituent effect between the CHO and CN group. For the low EA, i.e., high SOMO, ring density compounds CHO leads to a significantly higher EA than CN, while for the high electron affinity compounds and nitrobenzene-X the "normal" order,¹⁰ CN

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(8) Grimsrud¹ provides a general survey of initial results; Grimsrud² deals with the EA of SF₆ and C₇F₁₄ and with thermal electron detachment from azulene. Chowdhury³ provides measurements of ΔS_1° changes, Chowdhury⁴ the EA of perfluorobenzenes, Chowdhury⁵ the EA of cyano compounds, Chowdhury⁶ the EA of benzenes and naphthalenes, and Heinis⁷ the EA of anthracenes.

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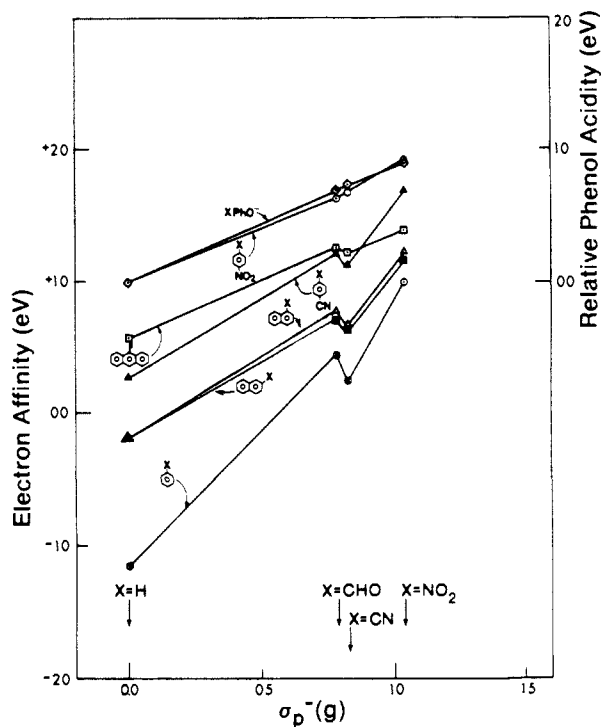
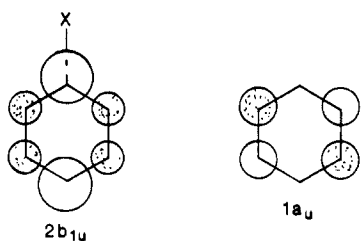


Figure 1. Electron affinities of benzenes, naphthalenes, anthracenes, cyanobenzenes, and nitrobenzenes with substituents X (H, HCO, CN, NO₂), vs. Hammett-type substituent constants σ_p^- (g) based on gas-phase acidities of phenols, PhOH; see Taft.¹⁰ The free energy change for the proton transfer $\text{PhO}^- + \text{X-PhOH} = \text{PhOH} + \text{X-PhO}^-$ is shown on the right-side ordinate. Electron affinities for benzaldehyde and benzonitrile are from Chen and Wentworth,^{9a,b} benzene and naphthalene from Jordan,^{9c,d} and other values from present laboratory.

stronger than CHO, electron-withdrawing effect is observed; see Figure 1.

The Hückel type SOMO orbitals for the benzene negative ion are shown as



Radom¹² has performed STO-3G calculations for several singly substituted benzene radical anions. He points out that electron-withdrawing substituents like CHO, CN, and NO₂ will lead to preference for the $2b_{1u}$ π^* orbital as the SOMO orbital since this orbital has high electron density in the ipso position of the substituent, whereas the otherwise equivalent $1a_u$ orbital has a node and thus zero electron density at this position. This means that the $2b_{1u}$ orbital can much better provide π -type electrons to feed the π -electron-withdrawing X and also provide nearby electron charge to interact with the dipole of X (field effect). The calculations of Radom¹³ predict, for the benzo anions $\text{C}_6\text{H}_5\text{X}^-$, a higher SOMO electron density on X = CHO (0.528e) relative to X = CN (0.160e). The separation of Taft and co-workers¹⁰ of the substituent effect (Table V, ref 10) into resonance R and inductive I effects, based on phenol gas-phase acidities and calculations, assigns a large-electron-withdrawing R effect (-9.2) and a small-electron-withdrawing I (-6.6) effect to CHO group,

while for CN the opposite assignment of a small R (-4.5) and a large I (-12.1) is made. We note that the larger R effect for CHO is parallel to the Radom-calculated larger SOMO π density for the CHO group of the benzaldehyde anion relative to CN in the benzonitrile anion.

The observation that the CHO substituent has a stronger stabilizing effect relative to CN in the radical anions with large SOMO π^* electron densities in the ring and the reversal of the effect as the density is decreased, see Figure 1, indicate that the π withdrawal (R effect) is much more strongly attenuated with decreasing SOMO ring density than the inductive effect. Since the I effect is largely an electrostatic field effect,¹³ which for the radical anions corresponds to a stabilization due to the attraction between the dipole of the substituent and the SOMO electron charge outside the substituent, the electrostatic energy terms could in principle be evaluated by calculation.¹⁴ Further experimental confirmation of the above observations is available from measured electron affinities⁶ of nitrobenzenes and cyanobenzenes substituted with a larger variety of substituents. These show that substituents whose effect is mostly due to a field-inductive stabilization, e.g., CF₃, increase the electron affinity of cyano- and nitrobenzene by nearly an equal amount.

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Hybridization Effects on Metal-Ligand Bond Lengths in Organometallic Compounds

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Single bonds to sp^2 -hybridized carbon centers are shorter than those to sp^3 centers, and linkages to sp carbons are shorter still. The phenomenon is general and well documented.¹ The theoretical² and experimental data in Table I illustrate the magnitude of the effect for bonds between carbon in its three common hybridization states and hydrogen, methyl, fluoro, silyl, and chloro substituents. Bond-length reductions are less for rehybridization from sp^3 to sp^2 carbon than from sp^2 to sp , consistent with a lesser change in p character, i.e., 25% to 33% vs. 33% to 50%.

Bond-length changes resulting from rehybridization at carbon may be attributed to differences in the radial extensions of valence s- and p-type orbitals, specifically the fact that valence p functions are more diffuse than the corresponding s-type functions. In this paper, we suggest that these same principles apply to the description of the bonding in transition-metal organometallic compounds.

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