decene (a mixture of cis and trans isomers), 3,3-dimethyl-1-butene, and undecylenic acid (Aldrich) were used as supplied. Mercuric acetate and sodium dichromate dihydrate (Mallinckrodt), trifluoroacetic acid (Matheson Coleman and Bell), gold(III) chloride, palladium(II) chloride, and thallium(I) acetate (Fisher Scientific), and rhodium(III) chloride (Alfa) were used without further purification. Elemental analyses were performed by Robertson Laboratory, Florham Park, N.J.

Mercuric Propionate. Red mercuric oxide (108 g) was added in 10-g portions to 100 ml of hot propionic acid. The oxide dissolved, giving a slightly yellowish solution which was filtered and allowed to cool to room temperature. The resulting crystals were recrystallized from propionic acid, washed with cold, dry acetone, and dried under vacuum (0.04 mm) at room temperature for 24 hr. The yield of product was 168.7 g (97%) as white needles having mp 114–116°.

General Procedure for the Mercury(II)-Catalyzed Oxidation of Olefins. Method A. To a 500-ml erlenmeyer flask was added 22.0 g (74 mmol) of sodium dichromate dihydrate, 50 ml of water, and 300 ml of dioxane. With stirring, 6.8 g (20 mmol) of mercuric propionate and 35 ml of trifluoroacetic acid were added. The dark orange-red solution was stirred until the salts had dissolved (ca 10 min), and the flask was placed in a water bath. With continued stirring, 100 mmol of olefin was added. The solution became dark and warm; ice was added as necessary to maintain the temperature at 25 ± 5°. The solution was stirred for 18 hr, poured into water (300 ml), and extracted with hexane (3 × 75 ml). The combined extracts were washed with water (3 × 50 ml), saturated sodium chloride solution (1 × 50 ml), and water (1 × 50 ml) and dried (MgSO$_4$).

General Procedure for the Mercury(II)-Catalyzed Oxidation of Olefins. Method B. To a 500-ml erlenmeyer flask was added 200 ml of acetone, 5 ml of water, and 6.8 g (20 mmol) of mercuric propionate. The flask was placed in a water bath and, with stirring, 100 mmol of olefin was added to the bright yellow solution. Jones reagent[7] (2*M*, 75 ml) was added dropwise during 4 hr. Ice was added as necessary to maintain the temperature at 25 ± 5°. The dark greenish-brown solution was stirred for an additional 4 hr and then poured into water (200 ml) and extracted with diethyl ether (3 × 75 ml). The combined extracts were washed with water (3 × 50 ml), saturated sodium chloride solution (1 × 50 ml), and water (1 × 50 ml) and dried (MgSO$_4$).

References and Notes

(1) Supported by the National Science Foundation, Grant MPS74-20946.

(2) John M. Lyons Fellow, 1972–1974.

(3) Studies of the mechanism and synthetic applications of the Wacker oxidation have been reviewed: E. W. Stern in "Transition Metals in Homogeneous Catalysis", G. Schrauzer, Ed., Marcel Dekker, New York, N.Y., 1972, Chapter 4. Despite the attention devoted to this reaction, there are no fully convincing answers to a number of important questions concerning its mechanism: viz., does the attacking oxygen nucleophile add to the olefin cis or trans to the palladium center? What are the details of the sequence of palladium hydride elimination–addition reactions that generates product? Is Pd(0) ever present in the catalytic Wacker oxidation, or is it palladium(II) hydride that is oxidized by Cu(II)?

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Intramolecular van der Waals–London Cohesions and Chemical Properties. Acid Weakening by Halogens and Related Effects.

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Substituent effects arising from intramolecular van der Waals–London attractions are examined. For substituents adjacent to reaction centers at which a single bond is converted into a double bond, or close to a site acquiring a charge, order-of-magnitude calculations (using London's formula) show appreciable stabilization of the new unsaturated species, or the species that has gained a negative charge, or lost a positive one, and increasing in the sequence $F < Cl < Br \simeq H < I < Me$.

Stabilization of anions, and destabilization of cations, by halogen substituents bound to sp^2-hybridized C atoms, which increases in the order $F < H < Cl < Br < I$ (or roughly this order), has long been known for aromatic compounds in aqueous media.[1-3] This order is prominent in the acidities, in water, of some α-halogeno nitroalkanes[4-6] forming anions X–C(Y)=NO$_2^-$ (see Table I); i.e., effects opposing the normal inductive effect (acid strengthening by X: $H \ll I < Br < Cl < F$) are important here. The (exceptionally) large anion destabilization by F (relative to H) in F–C(Y)=NO$_2^-$ [4,5] has been attributed[4] to (a) an increase in the order $I < Br < Cl < F$ in the sum of mesomeric electron donation by Hal and Hal p-electron–π-electron repulsions (both are zero for H), (b) a weakening of the C–F bond on changing from sp^3 to sp^2 hybridization, (c) double bond–no bond resonance effects. However, much evidence militates, in turn, against each of these explanations: (a)[7] e.g.[2a,d] the ionization potentials[8] of compounds Hal–CH=CH$_2$ and Hal–C$_6$H$_5$ [IP lowest for iodides; i.e. electron donation plus repulsion greatest with I; ICH(NO$_2$)$_2$ should be the weakest HalCH(NO$_2$)$_2$ acid]; (b) C–F bond lengths,[2a,d] $r(\text{F–C}_{sp^2}) < r(\text{F–C}_{sp^3})$; (c) numerous instances where F is greatly acid strengthening despite[2a,d] similar possibilities of double bond–no bond resonance.

In addition, in compounds Me–CHYNO$_2$, Me is acid *weakening*[9] unless Y is strongly electron withdrawing—a very rare situation for Me attached to an sp^2-hybridized atom.

This article deals with a relevant and neglected nonpolar substituent effect, viz., intramolecular van der Waals–Lon-

Table I
Ionization Constants of Nitroalkanes

Nitroalkane[d]	pK_a[a]		Nitroalkane[e]	pK_a[a]	
	Obsd[b]	Corr		Obsd[b]	Corr
HCH_2NO_2	10.21	10.7	$HCH(NO_2)_2$	3.6_3	3.9_3
F_2CHNO_2[c]	12.4		$FCH(NO_2)_2$	7.70	
$ClCH_2NO_2$	7.2_2	7.5_2	$ClCH(NO_2)_2$	3.80	
$BrCH_2NO_2$	8.2	8.5	$BrCH(NO_2)_2$	3.58	
$MeCHBrNO_2$[c]	7.3		$ICH(NO_2)_2$	3.19	
$MeCH_2NO_2$	8.5	8.8	$MeCH(NO_2)_2$	5.30	
Me_2CHNO_2	7.7				
$FCHClNO_2$	10.14				
$MeCHClNO_2$	6.8				

[a] If the number of ionizable hydrogen atoms (n) exceeds one, a statistical correction (log n) has to be added. [b] Data from ref 4, 5, 6, and 9. [c] No data available for FCH_2NO_2 or ICH_2NO_2. [d] Registry no. are, respectively, 75-52-5, 1493-05-6, 1794-84-9, 563-70-2, 563-97-3, 79-24-3, 79-46-9, 2375-33-9, 598-92-5. [e] Registry no. are, respectively, 625-76-3, 7182-87-8, 921-13-1, 996-67-8, 29610-14-8, 600-40-8.

don attraction. The stabilizations produced by this are proportional to the products of the polarizabilities of the interacting units, and inversely proportional to about the sixth power of the separations between them (see eq 1). Order-of-magnitude calculations for various substituents X in systems such as $XCH{=}NO_2^-$ give an increase in stabilization in the order $F < Cl < Br \simeq H < I < Me$.

Qualitatively, the relevant rules are: (*1*) *any chemical change in which a molecular moiety becomes more polarizable is facilitated increasingly as the polarizability of the substituent*[10] *increases.* Loss of a positive charge or acquisition of a negative one raises the polarizability (denoted by α) by[11] ca. 0.5 Å^3 per atom or molecule [principally at the charge center, but in part also for other nearby electrons (as these, too, are held less firmly after loss of a proton; and on account of the Silberstein[12b] effect—normally mutual exaltation of polarizability)]. Also, conversion of a pair of CH bonding electrons into a CC π-electron pair raises α by ca. 0.5 Å^3 (from 0.65 Å^3 to 1.15 Å^3).[2a,d] Hence, *an increase in the polarizability of a substituent* (*2*) *obstructs cation formation,* (*3*) *assists anion formation, and* (*4*) *results in an increased preference by the substituent for attachment to an* sp^2*- rather than an* sp^3*-hybridized atom.*

Quantitative treatment is difficult, but a basis for semiquantitative calculations is provided by London's formula (eq 1)[12] for the cohesion energy E_L for a pair of interacting units (A and B), where h is Planck's constant, I_A, I_B, α_A, and α_B are respectively the ionization potentials and polarizabilities of A and B, and R is the distance between the centers of their oscillating dipoles.

$$E_L = -\frac{3}{2}h\frac{I_A I_B}{I_A + I_B}\frac{\alpha_A \alpha_B}{R^6} \qquad (1)$$

Interactions at close range, within molecules with many (and different) units, present numerous problems. Chiefly, formula 1 is good, and the dependence on $1/R^6$ holds accurately only at long distances R. At short distances R, an appreciable interelectronic repulsion which also depends on α_A, α_B, and R, and which is difficult to estimate, is not allowed for by formula 1. It is proposed to overcome this by use of a net cohesion energy E_L^* (E_L minus the repulsion energy). A reasonable value[2c] for E_L^* is ca. $\frac{1}{2}E_L$ if $0.507(\alpha_A^{1/4} + \alpha_B^{1/4})/R$ is in the range of ca. 0.6–0.7 [but if this quantity > ca. 0.7, the ratio E_L^*/E_L diminishes rapidly; $0.507\alpha^{1/4}$ is the approximate (average) zero-point electronic oscillation amplitude[2e] in London's simplified oscillator[12a]]. Further, α_A and α_B will ordinarily be orientation dependent,[11b] and the complexity of the orientation averaging required, and the absence of strict pairwise additivity, precludes accurate calculations of intramolecular interactions. In the present work only the principal interaction of interest within a molecule, and its change in the reaction concerned, has been calculated, and anisotropy in α was neglected.[2c]

The units, normally, are electron pairs, and the interactions of importance, usually, are those between *adjacent* electron pairs; e.g. in the π-electron–CF interaction in $FCH{=}CH_2$ the C–F bonding electrons make the main contribution, and the nonbonding electrons on F are too far away to have much effect.

The values of I and α per electron pair here used were estimated from those observed for simple model compounds, and some assumptions,[2d] but the uncertainties introduced are expected to be relatively minor. The estimation of R can be difficult. The centers of the *oscillating* dipoles, taken to be the centroids of the electron pair clouds (not nuclear positions!), are given (or roughly given) by[2c] by symmetry for C=C and C–C bonds, and known from X-ray diffraction results[13] for C–H bonds. However, for C–Hal bonds their locations had to be estimated from dipole moment data.[2c] There is thus a sizable uncertainty in the numerical values of R^6 used, in addition to that about the analytic dependence of E_L^* on R. The size of the total margin of error in the absolute magnitude of E_L^* is not known.

The chemical changes treated were

$$XCH_2NO_2 \rightleftharpoons XCH{=}N^+({-}O^-)_2 + H^+ \quad X = H, Hal, or Me \qquad (I)$$

$$p\text{-}XC_6H_4N^+H_3\ (\text{or } p\text{-}XC_6H_4OH) \rightleftharpoons p\text{-}XC_6H_4NH_2\ (\text{or } p\text{-}XC_6H_4O^-) + H^+ \qquad (II)$$

For α and I for the π electrons in $CH_2{=}NO_2^-$ the $CH_2{=}CH_2$ values were taken, approximate cancellation of the effect of the positive charge on N and of the two (more distant) negative ones on O being assumed (giving rise also to approximately central positioning of the C=N π electrons); the internuclear distance r(C=N) used was 1.29 Å^3.[2a,c] The change in E_L (ΔE_L) was calculated for the interaction between the C–X bonding electrons and the electrons which, in the dissociation reaction (I), are converted from C–H into π electrons. The reduction in (the relevant) R^6 on dissociation was ignored to avoid overestimating of ΔE_L.

For reaction II the approach was different. The interactions (by X) of importance were taken to be those between the C–X bonding and four adjacent C–C σ *as well as* two adjacent π electrons. Acquisition of a positive charge by NH_2, or loss of a negative one by O^-, by protonation, pulls the latter six electrons away from C–X, and is estimated[2a,c]

Table II
Main Components of Cohesion Energies E_L, and Changes Therein on Ionization ΔE_L (Kilocalories/Mole)

Group X	H	F	Cl	Br	I	Me
$\alpha_B{}^{a,b}$	0.65	0.16	0.65	0.91	1.41	0.56
$r(\text{C–}c\text{CX})^{a,c,d}$	0.95	0.87^{i}	1.05	1.05	1.05	0.75
Values for Nitronate Ions,^{a,e} and ΔE_L for Deprotonation Reaction (I)						
$hI_AI_B/(I_A + I_B)^{a,f}$	5.81	6.02	5.62	5.52	5.42	5.51
$R^{a,d}$	1.39	1.31	1.48	1.48	1.48	1.21
$0.507(\alpha_A{}^{1/4} + \alpha_B{}^{1/4})/R^{g}$	0.71	0.64	0.66	0.70	0.73	0.79
$-E_L{}^{g}$	21.1	7.4^{i}	13.9	19.0	28.9	39.7
$-E_L{}^{*g}$	10.5	3.7	7.0	8.5	13	14?
$-\Delta E_L{}^{*g}$	4.6	1.6^{i}	3.0	4.1	5.7	6?
ΔE_L for Deprotonation Reaction (II)^{a,h}						
$-\Delta E_L{}^{g}$	1.13	0.47	0.81	1.11	1.7	2.6
$-\Delta E_L{}^{*g}$	0.56	0.23	0.40	0.55	0.8	0.9

[a] See ref 2b. [b] In Å^3 per (bonding) electron pair. [c] Distance from charge centroid of C–X bonding electrons to C nucleus. [d] In Å. [e] α_A for π electrons, taken as 1.15 Å^3. [f] In electron volts. [g] E_L and ΔE_L by formula 1; $E_L{}^*$ and $\Delta E_L{}^*$ estimated from these,[h] having special regard where necessary to the index of repulsion $0.507(\alpha_A{}^{1/4} + \alpha_B{}^{1/4})/R$; the minus sign denotes attraction, or gain therein. [h] See text. [i] A reduction by ¼ in the assessed CF bond moment gives $r(\text{C–}c\text{CX}) = 0.82$ Å, $E_L = -9.2$, and $\Delta E_L{}^* = 2.0$ kcal/mol.

to *raise* (the mean) R for these interactions by about 0.01 Å; i.e., a change of R, rather than that in α, is used in the calculation of ΔE_L.

The results obtained with eq 1[14] are shown in Table II (as are some of the quantities used in the calculation[2b]). These cohesion energies $E_L{}^*$, and the substituent effect on $E_L{}^*$, are substantial. The substituent effects on the changes $\Delta E_L{}^*$ on (de)protonation are appreciable when compared with the substituent effects on the free energies (ΔG) of (de)protonation observed in aqueous medium, for both reaction I and II.[1,2a]

Put in the simplest qualitative terms, as far as $E_L{}^*$ is concerned F is acid weakening relative to H because the polarizability of the C–F bonding electrons is only about a quarter of that of the C–H electrons, and Me is acid strengthening because the C–C (σ) bonding electrons are much closer to the nucleus of the sp^2-hybridized C atom (and hence to the π electrons) than are the CH electrons (see values for electron centroid–nucleus separations, and for R, in Table II).

Meaningful quantitative comparisons of calculated substituent effects on $E_L{}^*$ with inductive effects (e.g., monopole–permanent dipole interactions) or inductomeric effects [e.g., monopole–induced (permanent) dipole interactions] are hardly practicable at present.[15] The absolute values of $E_L{}^*$ are too uncertain, and the *uni*directional polarizabilities required for the calculation of induction effects in unsymmetrical bonds are not available. However, in the ionization (I), the N$^+$ atom moves closer to X while a negative charge is acquired farther away; this partial cancellation of charge fields experienced by X reduces the importance of polar effects, e.g., inductive and inductomeric, and substituent effects on $\Delta E_L{}^*$ are brought more to the fore.[17]

Intramolecular van der Waals–London attraction should have appreciable effects on many other properties,[2] e.g., in the acid strengthening and base weakening (relative to H) produced by unsaturated groups, and by many ortho substituents in benzene rings; also on bond lengths and heats of formation.

Comparisons of heats of formation of alkenes $C_2H_{4-n}X_n$ with those of their hydrogenation products $C_2H_{6-n}X_n$ give a measure of the preference by X for attachment to an sp^2 rather than an sp^3 C atom. The relevant quantity, $n^{-1} \times \{[\Delta H_f(\text{parent alkene}) - \Delta H_f(\text{substituted alkene})] - [\Delta H_f(\text{parent alkane}) - \Delta H_f(\text{substituted alkane})]\}$, while varying somewhat with n (and relative group dispositions, in cases of multiple substitution), appears to increase in the order F < Cl < H < Br < Me. This quantity (zero by definition for X = H) is always negative for F and positive for Me; the data,[18] unfortunately, are unsystematic, and in the range Cl, H, Br, where the differences are small, of uncertain reliability. Substituent effects on $E_L{}^*$ are probably the main factor in producing this sequence of preference for sp^2 attachment.

Supplementary Material Available. A fuller treatment will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.50 for photocopy or \$2.50 for microfiche, referring to code number JOC-75-3580.

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(15) E.g., it is not practicable to estimate by calculation the extent to which the inductomeric effect of Hal and the effect of Hal on $\Delta E_L{}^*$ contribute to the gas-phase acid strength sequence[16] $H\text{-}CH_2CO_2H \ll F\text{-}CH_2CO_2H < Cl\text{-}CH_2CO_2H < Br\text{-}CH_2CO_2H$ (in principle, both contribute to the observed halogen order, even though the inductomeric effect is expected to be the more important here). (NB The "anti-inductive" order is less prominent in $HalCH_2COOH$ than in $HalC_6H_4OH$ acidities.)

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Resonance Theory. VIII. Reactivities of Benzenoid Hydrocarbons

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An algorithm, logarithm of the number of Kekulé structures, gives resonance energies for benzenoid hydrocarbons that are equivalent to results of highly parameterized SCF–LCAO–MO calculations. The relationship also holds for odd alternant cationic and anionic species. Reactivity indices based on the structure count algorithm correlate with various types of experimental reactivity data.

A simple parameterized structure–resonance theory has recently been developed[1,2] that allows one to calculate resonance energies for many types of π-molecular systems that correlate precisely with the results of semiempirical SCF–MO (Dewar[3]) calculations, or with those obtained from open chain reference structure modified Hückel MO (Hess and Schaad[4]) procedures. During the course of that development an exponential relationship between the Kekulé structure count (SC) and the Dewar resonance energy was noted.[5] The purpose of this paper is to show that this relationship extends to cations and anions postulated as intermediates in reactions of benzenoid aromatic hydrocarbons. Consequently, accurate correlations and predictions of reactivities are quickly and precisely obtainable.

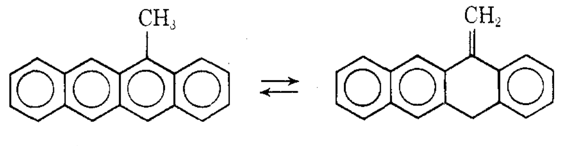
No attempt will be made here to give a quantum mechanical interpretation of the relationships described. A sufficient justification is the excellent quantitative agreement of experimental and theoretical data with the empirical SC function. However, it should be noted that the high correlative accuracy cannot arise from accidental or mathematical congruities[6] of resonance theory with the HMO formulation. HMO reactivity indices have been shown in most cases to yield poor correlations of reactivity data in comparison to the results of SCF calculations. Some illustrations of this fact will be given in tables to follow.

Resonance Energies of Benzenoid Hydrocarbons. The variable β and bond length SCF calculations, parameterized with thermochemical data, of Dewar and coworkers[3] can be taken to provide a reliable reference set of resonance energies. As shown previously,[5] there is an exact linear relationship between the logarithm of the SC and the Dewar[3b] resonance energy (RE) given in eq 1. Alternant and nonalternant benzenoid hydrocarbons, including compounds with essential single bonds, are included in the correlation.

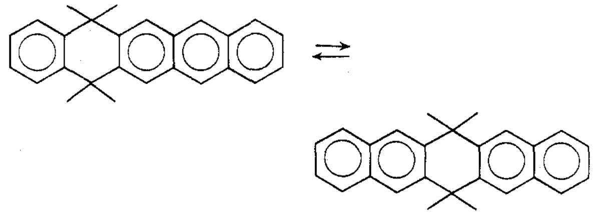
$$\mathrm{RE\ (eV)} = 1.185 \ln \mathrm{SC} \qquad (1)$$

Their structures were enumerated using the graph-theoretical methods described previously.[7] The correlation coefficient of the calculated resonance energies is 0.998, and the average deviation of the SC algorithm from the SCF result is ±0.042 eV, less than 1 kcal.

The calculations for acene derivatives summarized in Table I provide a stringent test of the SC algorithm. The SCF results were obtained by Herr[8] in an attempt to understand tautomeric equilibria of the types shown in eq 2 and 3. Assuming that the enthalpy differences between pairs of molecules are constant except for π energy differences, the energy of reaction, ΔE_π, should be a linear function of the logarithm of the ratio, SC of product P to SC of reactant R; cf. eq 4.



(2)



(3)

$$E = a(\ln \mathrm{SC_P} - \ln \mathrm{SC_R}) + b = a \ln (\mathrm{SC_P}/\mathrm{SC_R}) + b \qquad (4)$$

The structure count function parallels the calculated SCF energy differences very closely as evidenced by the correlation coefficients for the two groups of reactions, 1.000 and 0.990, respectively.

Some kinetic data suitable for testing eq 1 and 4 have been published by Dewar and Pyron.[9] They determined the rate of Diels–Alder addition of maleic anhydride to the aromatic compounds listed in Table II. The logarithm of the SC ratio is obviously a paralocalization energy and is highly correlated with the logarithm of the second-order rate constant, supporting the postulation of a cyclic transition state for the cycloaddition reaction. A calculation based on the assumption of rate-determining formation of a biradical intermediate (see next section) only gives a correlation coefficient of 0.738, in complete agreement with the prior SCF calculations and conclusions.[9]

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