tert-butoxide and appropriate amounts (by volume) of *tert*-butyl alcohol and DMSO.

Reaction Procedure.—Reactions of 2-butyl halides with potassium phenoxide and alkoxides in alcohols,[3b] and with bases in dipolar aprotic solvents and *tert*-butyl alcohol–DMSO mixtures,[3a] were conducted and elimination products were analyzed as before.

Control Experiments.—Negligible amounts of butenes (determined by glpc) were formed in the reaction of 2-butyl iodide (starting material most prone to E1 reaction) with an equivalent amount of 2,6-lutidine (sterically hindered base, present to inhibit acid-catalyzed reaction) in *tert*-butyl alcohol at 50° for 24 hr.

Reaction of 2-butyl iodide with varying concentrations of potassium phenoxide in ethanol in the presence of excess phenol gave the following olefinic proportions ([PhOK], [PhOH], % 1-butene, % *trans*-2-butene % *cis*-2-butene): 0.05 M, 1.05 M, 7.8 ± 0.2, 72.3 ± 0.2, 19.9 ± 0.1; 0.10 M, 1.00 M, 7.9 ± 0.3, 72.1 ± 0.6, 20.0 ± 0.3; 0.15 M, 0.95 M, 8.0 ± 0.2, 71.6 ± 0.2, 20.4 ± 0.4. Within experimental error, the relative amounts of butenes are invariant, indicating the absence of significant ethoxide ion promoted elimination. Based upon the pK_a's of ethanol and phenol in ethanol,[10] less than 1% of ethoxide is calculated to be present in an ethanolic solution of 0.1 M phenoxide and 1.0 M phenol.

Registry No.—2-Iodobutane, 513-48-4; 2-bromobutane, 78-76-2; 2-chlorobutane, 78-86-4.

(10) B. D. England and D. A. House, *J. Chem. Soc.*, 4421 (1962).

A Discussion of Inductive, Conjugative, and Steric Strain Effects on Polarographic Reduction Potentials of a Series of Biphenyl- and Phenanthrene-Related Compounds[1]

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In this study are reported the polarographic half-wave reduction potentials in dimethylformamide of a series of alkyl-substituted phenanthrenes and biphenyls. The shifts in the half-wave potential *vis-à-vis* the unsubstituted parent compounds are discussed in terms of hyperconjugative, inductive, and steric strain effects. Using the inductive model for alkyl substitution and making suitable correction for the hyperconjugative effect, correlation of half-wave potential shifts with HMO coefficients is attempted. Deviations from the expected correlation are explained in terms of steric interactions, and a semiquantitative estimate of these interactions is presented.

There has been rather sustained interest in recent years in the effects that substituent alkyl groups have on the physical and chemical properties of fused and bridged aromatic hydrocarbons. Changes in electronic spectra,[3-7] polarographic half-wave potentials ($E_{1/2}$),[6-11] and ionization potentials[7,12] have been discussed. In certain cases, such as that of biphenyl, the steric requirements of substitution can result in a change in the planarity of one part of the conjugated system relative to the rest of the molecule. Such perturbations of the conjugative resonance interaction have been shown to result in shifts of the so-called ultraviolet conjugation band (~250 nm)[3-5,11,13] and in shifts of polarographic $E_{1/2}$ values.[10,11]

Where rigid conjugated systems, such as fluorenes and phenanthrenes, are involved, changes in planarity on substitution are not so significant. However, Streitwieser and Schwager[9] showed that, besides the normal inductive effect, hyperconjugative interaction of the added alkyl group with the π system of the aromatic parent compound constitutes an appreciable portion of the shift in $E_{1/2}$ when substitution is made at a site with a fairly large Hückel molecular orbital (HMO) coefficient (c). When a correction is made for the conjugative interaction, fairly successful correlation of $E_{1/2}$ shifts (with respect to the unsubstituted parent) with the HMO coefficients was obtained.[9] If the hyperconjugative interaction is neglected, the results are not so satisfactory.[8,9] Valenzuela and Bard have also shown hyperconjugation to be an important consideration.[14]

When the alkyl substituent takes the form of a bridge between two parts of a conjugated system (such as in fluorene and 9,10-dihydrophenanthrene) $\Delta E_{1/2}$ values are even more difficult to correlate with inductive effects alone.[8] Steric effects may be important in the $E_{1/2}$ shifts of these compounds, but in earlier studies they have either not been a major factor or they have not been considered where inconclusive results were obtained.[8]

In this investigation the reduction $E_{1/2}$ values of a series of biphenyl- and phenanthrene-related compounds (where the added substituent is an alkyl group) were obtained in dimethylformamide (DMF) media. All of the factors enumerated above have been considered, with particular attention paid to molecules possessing steric strain, and to those species where the alkyl substituent is a bridging group. For many molecules it was found that correlation of $E_{1/2}$ shifts (corrected for conjugation effects) with the inductive effect of the added alkyl group is far from successful. These deviations from the "normal" correlation behavior are equated to steric strain, and this strain is estimated semiquantitatively.

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(2) Chemistry Department, The University of Cincinnati, Cincinnati, Ohio 45221.

(3) G. H. Beaven, D. M. Hall, M. S. Lesslie, and E. E. Turner, *J. Chem. Soc.*, 854 (1952).

(4) G. H. Beaven, and G. R. Bird, *ibid.*, 131 (1954).

(5) E. A. Braude and W. F. Forbes, *ibid.*, 3776 (1955).

(6) A. Zweig, J. E. Lancaster, M. T. Neglia, and W. H. Jura, *J. Amer. Chem. Soc.*, **86**, 4130 (1964).

(7) E. S. Pysh and N. C. Yang, *ibid.*, **85**, 2124 (1963).

(8) R. Gerdil, and E. A. C. Lucken, *ibid.*, **88**, 733 (1966).

(9) A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2316 (1962).

(10) A. J. Bard, K. S. V. Santhanam, J. T. Maloy, J. Phelps, and L. O. Wheeler, *Discuss. Faraday Soc.*, 167 (1968).

(11) R. Dietz and M. E. Peover, *ibid.*, 154 (1968).

(12) A. Streitwieser, Jr., *J. Phys. Chem.*, **66**, 368 (1962).

(13) H. Suzuki, *Bull. Chem. Soc. Jap.*, **32**, 1340, 1350, 1357 (1959).

(14) J. A. Valenzuela and A. J. Bard, *J. Phys. Chem.*, **73**, 779 (1969).

Experimental Section

Instrumentation.—Polarograms were obtained using a three-electrode system based on the operational amplifier circuits of DeFord[15] and were recorded on an Electro Instruments Model 500 X-Y recorder without damping. The reference electrode employed for all measurements was an anodized silver wire immersed in a 0.01 *M* $AgClO_4$–0.1 *M* tetra-*n*-butylammonium perchlorate (TBAP) solution in DMF. The stability of this system has been discussed earlier.[16] Details of the construction of the reference and salt-bridge compartments have been given elsewhere.[17] Measured $E_{1/2}$ values are accurate to at least ±10 mV except for those above −3.2 V, as background breakdown begins to be significant in this region making determination of accurate values difficult. Procedures for deaeration of the solution have been elaborated in an earlier report.[18]

Chemicals and Solutions.—The DMF solvent was Matheson Coleman and Bell Spectroquality grade. Purification was effected by passing dried solvent (Linde Type 4A Molecular Sieves) through an approximately 4-ft column of Woelm alumina at a rate of about 15 drops per minute.[19] This method of purification resulted in a product as free of reducible impurities as that obtained by an earlier reported distillation procedure,[18] and it had the advantage of being a much easier and faster method.

Phenanthrene (purchased from Matheson Coleman and Bell), 4,5-methylenephenanthrene (4,5-MeP) (from Aldrich Chemical Company), fluorene (Baker photosensitizer grade), and 2-methylbiphenyl (K and K Laboratories) were used as received. Biphenyl was recrystallized by standard methods. The 4,5-methylene-9,10-dihydrophenanthrene (4,5-Me-9,10-DHP) was recrystallized from methanol and melted at 140–141°. The 9,10-dihydrophenanthrene (9,10-DHP), from K and K Laboratories, was recrystallized from ethanol at acetone–Dry Ice temperatures, filtered, and washed with cold ethanol. The solid, melting near room temperature, was stored over silica gel in a refrigerator. Pure samples of 2,7-dimethylphenanthrene (2,7-DMeP), 4,5-dimethylphenanthrene (4,5-DMeP), 2,4,5,7-tetramethylphenanthrene (2,4,5,7-TMeP), 3,4,5,6-tetramethylphenanthrene (3,4,5,6-TMeP), and 1,8-dimethylfluorene (1,8-DMeF) were obtained from Professor M. S. Newman (Department of Chemistry, Ohio State University, Columbus, Ohio).

Hydrocarbon solutions in DMF were 0.1 *M* in TBAP and millimolar in sample.

Results and Discussion

As is the usual practice, it is assumed that the electron added in the reduction process occupies the lowest unoccupied molecular orbital of the hydrocarbons. According to Streitwieser and Schwager,[9] a substituent alkyl group can be considered as making the carbon atom to which it is attached less electronegative by its electron-donating (inductive) ability. The altered coulomb integral can be defined as

$$\alpha_r = \alpha_0 + h_r\beta_0 \qquad (1)$$

where h_r is negative. The change in the energy, ϵ_{m+1}, of the lowest vacant molecular orbital is given by

$$\delta\epsilon_{m+1} = c^2{}_{m+1,\,r}\,\delta\alpha_r \qquad (2)$$

where $c_{m+1,\,r}$ is the coefficient of the *r*th atomic orbital in the $(m + 1)$st molecular orbital, the lowest vacant orbital. However as

$$\delta\alpha_r = \alpha_r - \alpha_0 = h_r\beta_0 \qquad (3)$$

$$\delta\epsilon_{m+1} = c^2{}_{m+1,\,r}\,h_r\beta_0 \qquad (4)$$

The result is that the inductive effect raises the energy of the vacant orbital and shifts $E_{1/2}$ to more negative potentials. It is also expected that inductive effects are additive so that if more than one alkyl group is involved then

$$\delta\epsilon_{m+1,\,r} = \sum_r c^2{}_{m+1,\,r}\,h_r\beta_0 \qquad (5)$$

Therefore a linear correlation of shifts of half-wave reduction potentials from those of the unsubstituted compound with $\Sigma_r c^2{}_{m+1,\,r}$ should be obtained in this case. It is assumed that the c_{m+1} values do not change on methyl substitution.

As mentioned earlier, Streitwieser and Schwager have shown that hyperconjugative interaction of the added alkyl group also may be an important factor in changes in $E_{1/2}$.[9] Correction for this effect is easily made, however, based on the assumption that the ultraviolet conjugation band, which is related to transitions of an electron from the highest occupied to the lowest vacant π-molecular orbital, is affected solely by conjugative and not by inductive effects.[9] Likewise, as the spatial geometry is assumed not to change during an electronic transition (Franck–Condon principle), shifts in the conjugation band ought not to reflect strain effects except as they give rise to changes in resonance interaction.[13] Therefore the bathochromic shift in the frequency of the conjugation band (ν parent–ν substituted) can be converted to volts (1 eV = 8066 cm^{-1}) and added to the measured $E_{1/2}$ values. This correction has been applied to all compounds in this study. Where significant deviation from the expected correlation behavior (where only hyperconjugative and inductive effects are present) is found, the cause is attributed to steric effects, as discussed below. Apparently steric strain is more extensive in the excited state than in the ground state, and the LVMO is raised in energy more than the HFMO.

Phenanthrene Related Compounds.—Polarographic and ultraviolet spectral data for phenanthrene and related compounds is given in Table I. Analysis of the polarograms showed them to be reversible, one-electron waves.[16,18] The $E_{1/2}$ of 4,5-MeP was corrected for the small anodic shift (about 20 mV) resulting from the self-protonation (ECE) sequence. This correction was estimated from the results of Janata and Mark.[16,20] Also given in Table I are the $c^2{}_{m+1,\,r}$ values for phenanthrene.

All of the compounds in this series are considered to be essentially planar, although some twist of the phenanthrene ring system occurs with substitution in the 4 and 5 positions.[21a] Even phenanthrene itself is somewhat strained because of proton–proton interaction at the 4 and 5 positions,[22] although some of the strain is relieved by a slight twist away from coplanarity.[21a]

In Figure 1 is shown the correlation of $E_{1/2}$ (corrected for conjugation effects) *vs.* $\Sigma_r c^2{}_{m+1,\,r}$ obtained by Streit-

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[15] (a) D. D. DeFord, Analytical Division, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., 1958; (b) W. M. Schwartz and I. Shain, *Anal. Chem.*, **35**, 1770 (1963).

[16] J. Janata and H. B. Mark, Jr., *J. Phys. Chem.*, **72**, 3616 (1968).

[17] J. R. Jezorek and H. B. Mark, Jr., *ibid.*, **74**, 1627 (1970).

[18] J. Janata, J. Gendell, R. C. Lawton, and H. B. Mark, Jr., *J. Amer. Chem. Soc.*, **90**, 5225 (1968).

[19] N. S. Moe, *Acta Chem. Scand.*, **21**, 1389 (1967).

[20] Estimates of the pK_a of this and other compounds in this study containing the methylene bridge range from 20 [C. D. Ritchie and R. E. Ushold, *J. Amer. Chem. Soc.*, **89**, 1721 (1967)] to 25 (A. Streitwieser, "Molecular Orbital Theory," Wiley, New York, N. Y., 1962, pp 414–415). A radical anion of the hydrocarbon is able to abstract a proton from another molecule of hydrocarbon at the electrode giving an anodic shift to $E_{1/2}$.

[21] (a) H. Suzuki, "Electronic Absorption Spectra and Geometry of Organic Molecules," Academic Press, New York, N. Y., 1967, pp 380–383; (b) p 287.

[22] A. Streitwieser, "Molecular Orbital Theory," Wiley, New York, N. Y., 1962, p 344.

Table I

Polarographic and Ultraviolet Spectral Data for Phenanthrenes in DMF

Compd	$E_{1/2}$, measured[a]	λ (nm)	ν (cm⁻¹)	From phenanthrene Δλ	From phenanthrene Δν	Correction, mV	$E_{1/2}$, corrected	$\Delta E_{1/2}$, corrected	$\Sigma c^2_{m+1,r}$ r	Spectral ref
Phenanthrene	−2.904	292.1	34,235							*b, c*
2,7-DMeP	−2.946	295	33,898	+2.9	−337	42	−2.988	84	0.004	*b*
4,5-DMeP	−2.814	312.5	32,020	+20.4	−2215	275	−3.089	185	0.108	*b*
4,5-MeP	−2.881	299	33,445	+7	−801	99	−3.000	96	0.054	*c*
	+20 mV								0.108	
	(ECE) = −2.901									
2,4,5,7-TMeP	−2.853	315.9	31,598	+23.8	−2637	327	−3.180	276	0.112	*d*
3,4,5,6-TMeP	−2.948	316.8	31,565	+24.7	−2670	332	−3.280	376	0.306	*d*

[a] Reference electrode is Ag/AgClO$_4$ (0.01 *M*) in DMF. [b] P. Nounou, *J. Chim. Phys. Physicochim. Biol.*, **64,** 276 (1967). [c] C. Karr, Jr., *Appl. Spectrosc.*, **13,** 15 (1959). [d] This work, in CH$_3$CN, Cary 14 spectrometer.

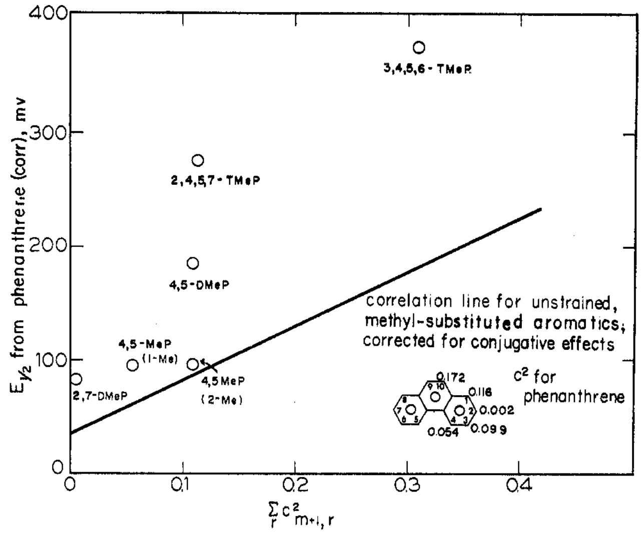

Figure 1.—Attempted correlation of polarographic half-wave potentials, corrected for conjugation, with the effect of alkyl substituents in phenanthrene using the inductive model. The solid line was obtained by Streitwieser for unstrained, methyl-substituted, alternant aromatic hydrocarbons.

wieser and Schwager for alkyl-substituted, unstrained, alternant aromatic hydrocarbons.[9] That this line does not go through the origin seems strange. Streitwieser and Schwager do not discuss this problem, and while Neikam and Desmond[23] also note the situation, they do not offer any explanation. However, the effect seems real, and the experimental correlation will be used. Results of the present study are then compared with this correlation line. Satisfactory fit is obtained for 2,7-DMeP and 4,5-MeP. The deviation of 4,5-DMeP from the purely inductive correlation line is about 100 mV. This is equivalent to about 2.3 kcal/mol of steric energy (1 eV = 23 kcal/mol) over and above that which is present in phenanthrene itself. When further substitution is made alongside the 4- and 5-methyl groups to give 3,4,5,6-TMeP, an even greater deviation is observed, equivalent to about 4.4 kcal/mol. The additional 2.1 kcal/mol results from methyl–methyl crowding in the 3,4 and 5,6 positions, as well as increased overlap of the 4- and 5-methyl groups, the so-called "buttressing effect" noted by Newman, *et al.*[24] The steric overlap of the 4- and 5-methyl groups is evident for 2,4 5,7-TMeP as well, but it seems as if other effects are present beyond this, as the deviation from the correlation is greater than the sum of those of 2,7-MeP and 4,5-MeP. A form of "buttressing" interaction is possible in the 2,3,4 and 5,6,7 positions, *i.e.*, methyl–proton–methyl crowding. Interactions of this type have been discussed by Braude and Forbes for meta substitution in biphenyl.[5]

Biphenyl and Related Compounds.—In Table II are given the polarographic and spectral data for biphenyl and substituted biphenyl compounds. Of these species biphenyl and 9,10-DHP deviate from planarity.[25] In order to relieve steric overlap in the ortho position, biphenyl is twisted about the bridging bond, while twisting in 9,10-DHP occurs in order that the sp^3 angles of the ethylene bridge be more closely accommodated.[3,5,13] A twist of up to 20° in both compounds has been shown to cause very little reduction in the π–π interaction of the aromatic rings compared to the hypothetical planar molecule.[26] Indeed the slight loss of resonance interaction is balanced by the decrease in steric overlap of the ortho protons.[5] For those compounds containing bridging methylene groups, the assumption is made that the $E_{1/2}$ shift of the self-ECE process is the same as that of 4,5-MeP, and a 20-mV correction is applied, as estimated from Janata and Mark.[16] In Figure 2 is shown the shift in $E_{1/2}$ (corrected for conjugation) *vis-à-vis* biphenyl, of the compounds under study, the experimentally determined correlation line of Streitwieser and Schwager,[9] and the c^2 values for biphenyl. Because some doubt exists as to whether a bridging methylene or ethylene group is equivalent to one or two substituent methyl groups, all possibilities have been considered. As mentioned above, the 2,2′-proton interaction of biphenyl is minimized with the twist about the bridging bond.[5,13] When the bridging methylene group is introduced between the 2 and 2′ positions to give fluorene, however, the ortho protons remaining are now forced into a strained, eclipsed conformation. The minimum deviation from the correlation line, using the rather doubtful assumption that the methylene group is considered to have the same effect as two methyl groups,[8] is equivalent to about 4.8 kcal/mol of steric strain compared to biphenyl itself.

That 4,5-DMeP seems to have less strain energy than fluorene, which has only two protons sterically interacting instead of two larger methyl groups, is understandable when it is remembered that this method of estimat-

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[23] W. C. Neikam and M. M. Desmond, *J. Amer. Chem. Soc.*, **86,** 4811 (1964).

[24] H. A. Karnes, B. D. Kybett, M. H. Wilson, J. L. Margrave, and M. S. Newman, *ibid.*, **87,** 5554 (1965).

[25] Braude and Forbes (ref 5) contend that 9,10-DHP, while twisted in the ground state, is nearly coplanar in the excited state. This contention is disputed by Suzuki (ref 13) who assumes no geometric rearrangement during an electronic transition according to the Franck–Condon principle.

[26] K. Ishizu, *Bull. Chem. Soc. Jap.*, **37,** 1093 (1964).

TABLE II

POLAROGRAPHIC AND ULTRAVIOLET SPECTRAL DATA FOR BIPHENYL AND SUBSTITUTED BIPHENYLS IN DMF

Compd	$E_{1/2}$, measured[a]	λ (nm)	ν (cm^{-1})	From biphenyl Δλ	Δν	Correction, mV	$E_{1/2}$, corrected	$\Delta E_{1/2}$, corrected	$\sum_r c^2_{m+1,r}$	Spectral ref
Biphenyl	−3.034	249.5	40,080							b
Fluorene	−3.123 +20 mV (ECE) = −3.143	261.5	38,241	+12	−1839	+228	−3.371	−337	0.089 0.178	b
9,10-DHP	−3.043	263.5	37,951	+14	−2129	+264	−3.307	−273	0.089 0.178	b, c
4,5-Me-9,10-DHP	−3.240 +20 mV (ECE) = −3.260	272	36,765	+22	−3315	+412	−3.652	−638	0.178 0.267 0.356	d
1,8-DMeF	−3.004 +20 mV (ECE) = −3.024	255.4	39,154	+5.9	−926	+115	−3.139	−105	0.127 0.216	e
2-Me-biphenyl	−3.202	235	42,548	−14.5	+2468	+52[f]	−3.254	−220	0.089	b
4-Me-biphenyl		253	39,525	+3.5	−555					b

[a] Reference electrode is Ag/AgClO$_4$ (0.01 *M*) in DMF. [b] Reference 13. [c] Reference 3. [d] R. N. Jones, *J. Amer. Chem. Soc.*, **63**, 1658 (1941). [e] This study, in CH$_3$CN, Cary 14 spectrometer. [f] Correction calculated from shift of 4-Me-biphenyl.

ing strain energies does not give "absolute" energies, but only yields a value with respect to the parent compound. In 4,5-DMeP two overlapping methyl groups are substituted for the two overlapping 4- and 5-position protons of phenanthrene. In fluorene two protons are brought into geometric interaction, whereas in biphenyl they are able to avoid each other *via* the twist of the molecule. In addition there is probably a certain amount of internal strain in the fluorene molecule as it is forced into a planar or near planar configuration.[3,13,21b] It may be that this "internal" ring strain is of the "hybridization effect" type discussed by Streitwieser,[27] whereby the ring juncture carbon atoms rehybridize to accommodate the small bond angles of the strained portion of the molecule. This situation results in an anodic shift to $E_{1/2}$, as discussed by Rieke, *et al.*, for some naphthalene base compounds[28] or the internal strain could be of a type which introduces a further cathodic shift to $E_{1/2}$ beyond that of spatial overlap of the ortho protons. It is also noticed that the bathochromic shift produced by hyperconjugation of the methylene bridge is considerably larger than one would expect even for two methyl groups. This large effect probably results from the possibility of stabilization of the hyperconjugated conformation by both phenyl rings, the liklihood of some π–π interaction of the phenyl rings through the methylene bridge,[5] and also from the planar structure which allows better conjugation across the bridging bond.[3,13,21b] The $E_{1/2}$ value of fluorene has been corrected for all these increases in conjugative interaction, *via* the uv shift, in order to yield the steric strain energy.

If an ethylene bridge is introduced across the ortho positions of biphenyl, yielding 9,10-DHP, the molecule is still allowed a measure of twist,[5] so that the remaining ortho protons are essentially staggered. However, the protons of the ethylene bridge may still be subject to some overlap as the ethylene carbon atoms may not be able to attain the full tetrahedral angle. The estimated strain energy of about 3.8 kcal/mol then seems reasonable for partial overlap of the remaining ortho protons and those of the ethylene bridge.

If the ortho protons of 9,10-DHP are replaced with a methylene bridge to give 4,5-Me-9,10-DHP, the molecule is forced to assume a planar configuration.[13] It is noted that the deviation from the correlation line for this compound is the most marked of any studied. The strain energy equivalent is about 9.8 kcal/mol. This energy can probably be traced in part to the interaction of the four ethylene protons which are now "locked" into an eclipsed configuration. The energy barrier for rotation of ethane from the staggered to the eclipsed conformation is about 3 kcal/mol.[29] Also probably contributing to the total is the fairly significant "internal" strain in the molecule as a whole, as the ethylene carbon atoms are not able to attain tetrahedral geometry because of the forced coplanar structure. The comments concerning the effect of this "internal" strain on $E_{1/2}$ which were made about fluorene are also applicable here. The very large "strain energy" found

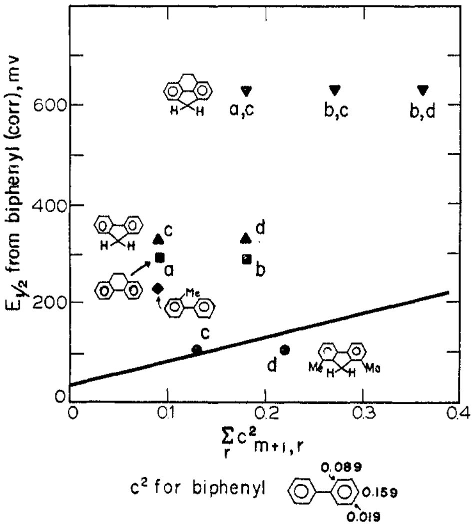

Figure 2.—Attempted correlation of polarographic half-wave potentials, corrected for conjugation, with the effect of alkyl substituents in biphenyl using the inductive model: (a) ethylene equivalent to one methyl group; (b) ethylene equivalent to two methyl groups; (c) methylene equivalent to one methyl group; (d) methylene equivalent to two methyl groups. The solid line is that obtained by Streitwieser for unstrained, methyl-substituted, alternant aromatic hydrocarbons.

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[27] A. Streitwieser, Jr., G. R. Ziegler, P. C. Mowery, A. Lewis, and R. G. Lawler, *J. Amer. Chem. Soc.*, **90**, 1357 (1968).

[28] R. D. Rieke, W. E. Rich, and T. H. Ridgway, *Tetrahedron Lett.*, 4381 (1969).

[29] C. R. Noller, "Chemistry of Organic Compounds," W. B. Saunders, Philadelphia, Pa., 1965, p 64.

would seem to indicate that a cathodic shift of $E_{1/2}$ is the result, not the anodic shifts observed by Rieke, *et al.*[28] The reason for a cathodic shift is not apparent at this time.

That 1,8-DMeF falls very close to the correlation line is perhaps surprising. However, this good correlation is actually indicative of the breakdown of the hyperconjugative correction procedure for this nonalternant hydrocarbon. In all other cases discussed so far, alkyl substitution has been seen to produce a shift of the ultraviolet conjugation band to lower energies, while substitution in the 1 and 8 positions of fluorene has the opposite effect. Sandorfy has stated that, for nonalternant hydrocarbons, methyl substitution can cause either bathochromic or hypsochromic shifts, depending on the position of substitution.[30] Despite the fact that, in this case, methyl substitution would be expected to yield a cathodic shift in addition to that resulting from the inductive effect, the actual measured $E_{1/2}$ is more anodic than that of fluorene itself. It appears then that the usual relationships between ultraviolet spectral and polarographic data do not hold for the nonalternant hydrocarbon fluorene.

The polarographic reduction potential for 2-methylbiphenyl has also been determined. However, the usual hyperconjugative correction is not possible because the shift of the conjugation band is composed of two components acting in opposite directions.[13] Conjugation of the methyl group with the biphenyl π system causes the typical bathochromic shift, while steric overlap of the ortho methyl with the ortho proton, resulting in increased twist about the bridging bond (58°),[13] causes a hypsochromic shift because of reduced $\pi-\pi$ interaction. (The decrease in resonance interaction across the bridging bond has been estimated by Braude and Forbes[5] to be 7 kcal/mol, but their interpretation has been strongly disputed by Suzuki.[13]) Therefore the hyperconjugative shift for 4-methylbiphenyl, multiplied by the ratio of the HMO coefficients for the 2 and 4 positions, has been applied as a correction to 2-methylbiphenyl. When this is done, $E_{1/2}$ falls about 145 mV above the correlation line, equivalent to a strain effect of about 3.3 kcal/mol. This energy results from methyl–proton interaction at the ortho position, as well as decreased $\pi-\pi$ interaction across the bridging bond with respect to biphenyl.

It is seen then that using the inductive model of alkyl substitution in alternant aromatic hydrocarbons, and applying an appropriate correction for hyperconjugative effects, a rough estimate of steric interaction can be obtained polarographically. It appears, however, as if this procedure is not valid for substituted nonalternant aromatic hydrocarbons such as fluorene.

Registry No.—Phenanthrene, 85-01-8; 2,7-DMeP 1576-69-8; 4,5-DMeP, 3674-69-9; 4,5-MeP, 203-64-5; 2,4,5,7-TMeP, 7396-38-5; 3,4,5,6-TMeP, 7343-06-8; biphenyl, 92-52-4; fluorene, 86-73-7; 9,10-DHP, 776-35-2; 4,5-Me-9,10-DHP, 27410-55-5; 1,8-DMeF, 1207-11-0; 2-methylbiphenyl, 643-58-3; 4-methylbiphenyl, 644-08-6.

Acknowledgments.—The authors wish to sincerely thank Professor M. S. Newman for the methyl-substituted phenanthrenes which he so kindly supplied, and Professor R. C. Lawton for helpful discussions.

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[30] C. Sandorfy, "Electronic Spectra and Quantum Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1964, p 344.

The Acetylation of Cyclooctene, 1,3-Cyclooctadiene, and 1,5-Cyclooctadiene

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The acetylation of the three title olefins in the presence of aluminum chloride and of stannic chloride, employing a variety of conditions, has been surveyed. Acetylation of cyclooctene using pure acetyl chloride and aluminum chloride gives mainly ring-contraction products reported earlier, whereas use of stannic chloride leads mainly to 1-acetyl-4-chlorocyclooctane and 4-acetylcyclooctene. Acetylation with acetic anhydride in several solvents gives mixtures of acetylchlorocyclooctane, acetoxycyclooctyl acetate, and acetylcyclooctenes. From the acetylation of 1,3-cyclooctadiene in the presence of stannic chloride, there was isolated 1-acetyl-4-chlorocyclooctene and a mixture of 1- and 2-acetyl-1,3-cyclooctadiene; aluminum chloride gives only tars. Acetylation of 1,5-cyclooctadiene using either catalyst produces 50–60% of 2-acetyl-6-chlorobicyclo[3.3.0]octane, which was degraded to bicyclo[3.3.0]octane-2,6-dione.

The Friedel–Crafts acylation of eight-membered cyclic olefins is of interest both as part of the chemistry of medium-ring compounds, a class noted for multitudinous rearrangements and transannular reactions,[2] and as a synthetic entry into substituted eight-carbon mono- and bicyclic systems. In an early investigation the reaction of acetyl chloride–stannic chloride with cyclooctene, followed by distillation of the product from base, was employed in the preparation of 1-acetylcyclooctene.[3] More recently, Jones, Taylor, and Rudd stated that aluminum chloride catalyzed acetylation of cyclooctene, followed by treatment with base, gave the same product.[4] This result was subsequently shown to be incorrect by two groups. We reported in preliminary fashion the finding that aluminum chloride catalyzed acetylation of cyclooctene gave 4-chloro-4-ethyl-1-acetylcyclohexane (40%) and 4-methyl-1-ace-

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[2] See, for example, V. Prelog and J. G. Traynham in "Molecular Rearrangements," Vol. I., P. DeMayo, Ed., Wiley, New York, N. Y., 1963, Chapter 9.

[3] L. Ruzicka and H. A. Boekenhoogen, *Helv. Chim. Acta*, **14**, 1319 (1931).

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