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THE EXPLORATION OF RESPONSE SURFACES FOR THE DETERMINATION OF HÜCKEL MOLECULAR ORBITAL PARAMETERS

PHENOL BLUE*

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Abstract—Simple Hückel molecular orbital (HMO) calculations on phenol blue using parameters given in the literature predict that the electron density on the oxygen atom decreases upon an $N \rightarrow V_1$ transition. This is in disagreement with the classical interpretation of light absorption of this molecule. From an examination of available experimental data, certain conclusions are drawn with which a molecular orbital treatment of phenol blue should agree. By exploring suitable response surfaces, a set of Coulomb integrals was determined which, in the Hückel approximation, gave agreement with current interpretations of the experimental data. The shift in λ_{max} of phenol blue and its α-naphthol analog by some simple substituents was calculated using this model. The results are in qualitative agreement with experiment. Two sets of phenol blue HMO parameters are examined by a semi-empirical, antisymmetrized molecular orbital calculation with limited configuration interaction.

INTRODUCTION

THE relative merits of Hückel molecular orbital (HMO) calculations *vs.* the more sophisticated self-consistent field (SCF) and antisymmetrized molecular orbitals with configuration interaction (ASMO CI) methods have been discussed quite thoroughly in the literature. It is known that the first method has the disadvantage that in it no account is taken of electron repulsion and hence some ambiguity enters in the choice of suitable *h*- and *k*-parameter values (Eqns. 1 and 2) for heteroatoms. With regard to the latter point, the problem has been succinctly stated by

$$\alpha_X = \alpha_0 + h_X\beta_0 \tag{1}$$

$$\beta_{CX} = k_{CX}\beta_0. \tag{2}$$

Streitwieser:[1] "The ideal procedure to evaluate these parameters would start with a correlation between some experimental property and a calculated quantity established for hydrocarbon systems and would follow with an application of this correlation to a number of compounds containing one or more of the heteroatoms under test with a systematic variation of h_X and k_{CX}. Such a procedure would not only determine the best values of these parameters to use with the correlation but would also reveal whether unique values exist . . . . Unfortunately, the ideal procedure has never been followed *in toto* and has only rarely even been used in part. More often, parameter values have been assigned as guesses partly based on theory or on the basis of applications of assumed validity. The result has been a profusion of parameter values in the literature."

The intent of this paper is, therefore, to present a method whereby, with a *minimum*

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* Communication No. 2330 from the Kodak Research Laboratories.

[1] Reprinted with permission from A. Streitwieser, Jr., *Molecular Orbital Theory for Organic Chemists* p. 117. John Wiley, New York, N.Y. (1961).

number of calculations, one may determine not only suitable parameters for a given class of compounds, but at the same time gain some insight into the *uniqueness* of the parameters. The method to be described permits the examination of an entire parameter space at once.

In a mathematical sense, quantities such as electron densities and bond orders are dependent variables, since they are observed as responses to particular values of independent variables. In HMO theory, the independent variables are the well-known Coulomb and resonance integrals. In the language of experimental design, the independent variables are known as factors and the dependent variables, as responses. In performing a Hückel molecular orbital calculation, one therefore determines the effect which certain factor levels (values of the Coulomb and resonance integrals) have upon various responses, such as the previously mentioned electron densities and bond orders. In practice what is often done is to choose several sets of factor levels and to determine the effect which these have upon the dependent response. By such a technique, however, it soon becomes apparent that, with a random choice of factor levels, only limited conclusions are possible regarding the effect which other factor levels would have upon the responses.

On the other hand, a properly designed experiment in which factor levels are chosen by established statistical methods permits a maximum of information to be obtained from a minimum of experimentation. Perhaps its chief drawback is that the minimum number of experiments may in fact be a rather large number. On the other hand by such a treatment a regression of a response (y) on the factor levels (x_1, x_2, . . .) may be carried out with the result that an equation of the form

$$y = b_0 + b_1x_1 + b_2x_2 + \ldots + b_{11}x_1^2 + b_{22}x_2^2 + b_{12}x_1x_2 + \ldots$$

may be derived, the degree of the equation depending upon the desired accuracy. Once such an equation has been derived, the effect upon y of any choice of x_1, x_2, . . . within the experimental design is readily determined. Provided the number of factors does not exceed three (although the principles apply equally well to any number of factors), a response may be plotted as a function of factor levels and, by connecting points of equal response, a response surface generated. Such a surface is of value to the experimenter, since he can now see at a glance the effect which the factor levels have upon the given response. The choice of factor levels for the experimental design and the application of the method to problems in other fields has been discussed in the literature.[2–5]

The compounds chosen for investigation are indoaniline dyes derived from phenols and α-naphthols, well known as the cyan image dyes of color photography. The parent dye of this class may be considered to be phenol blue (I). Solvent[6,7] and substituent[8–10] effects on the energy of the long-wavelength absorption maximum of

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[2] *The Design and Analysis of Industrial Experiments* (Edited by O. L. Davis) pp. 495–578. Hafner Publishing Co., New York, N.Y. (1954).

[3] G. E. P. Box and K. B. Wilson, *J. Roy. Statis. Soc.* **B13**, 1 (1951).

[4] G. E. P. Box, *Biometrics* **10**, 16 (1954).

[5] G. E. P. Box and J. S. Hunter, *Ann. Math. Stat.* **28**, 195 (1957).

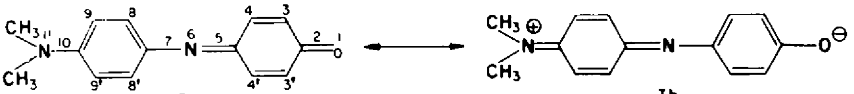
[6] L. G. S. Brooker and R. H. Sprague, *J. Amer. Chem. Soc.* **63**, 3214 (1941).

[7] E. G. McRae, *J. Phys. Chem.* **61**, 562 (1957).

[8] P. W. Vittum and G. H. Brown, *J. Amer. Chem. Soc.* **68**, 2235 (1946).

[9] C. R. Barr, G. H. Brown, J. R. Thirtle and A. Weissberger, *Phot. Sci. and Eng.* **5**, 195 (1961).

[10] A. P. Lurie, G. H. Brown, J. R. Thirtle and A. Weissberger, *J. Amer. Chem. Soc.* **83**, 5015 (1961).



Ia Ib

phenol blue[11] have led several workers to conclude that the first excited state (V_1) of this molecule receives a larger contribution from the polarized form, Ib, than does the ground state (N). An increase in solvent polarity or the introduction of hydrogen-bonding substituents *ortho* to the carbonyl results in a bathochromic shift of the $N \rightarrow V_1$ absorption maximum. McRae has shown[7] from the solvent effects that the dipole moment in the first excited state is greater than in the ground state.* Both the solvent and substituent effects are compatible with a lowering of the π-electronic energy of the more polar excited state relative to the ground state.

Simple Hückel molecular orbital calculations on phenol blue, using Coulomb integrals given in the literature,[12–15] do not, in general, agree with this interpretation of light absorption with regard to the change in electron density on oxygen (Δq_0). These calculations showed that $\Delta q_0 < 0$ for this transition. It was decided therefore to investigate systematically the effect upon certain responses (e.g., Δq_0, $\Delta q_{\dot{N}}$, $\Delta q_{\ddot{N}}$)† of varying the electronegativity parameters, h_x, of the three heteroatoms in phenol blue. Since electron densities are more readily affected by the choice of Coulomb than resonance integrals, the latter were assigned reasonable values and assumed to be constant throughout the calculations.

In addition to the Hückel MO calculations, a semi-empirical ASMO method with limited configuration interaction[16–19] was applied to phenol blue, using two different sets of starting MO's (v.i.). Although sufficient configuration interaction can correct any inadequacies in the choice of starting MO's, practical considerations, particularly in the case of large molecules, often limit the extent of configuration interaction which can be invoked. With limited configuration interaction, then, the results will still be partly determined by the choice of starting MO's. On the other hand, it was thought that the extent of energy lowering in a limited configuration interaction treatment, and the relative magnitudes of the resulting coefficients in the configurational wave functions should give some idea as to how close the starting MO's were to the self-consistent field LCAO MO's.

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* Although McRae calculated the excited state dipole moment on the basis of colinearity of the ground and excited state moments, the assumption of non-colinearity would require the length of the excited state moment to be even larger.

† Throughout this paper the symbolism of Streitwieser (Ref. 1) will be used to distinguish between nitrogen atoms which contribute one or two p-electrons to the π-system; $\dot{N}$ represents azomethine nitrogen; $\ddot{N}$, amino nitrogen.

[11] Although the numbering system used here for phenol and naphthol dyes is not the conventional one (Ref. 8), it is more convenient for molecular orbital calculations.

[12] Ref. (1), p. 135.

[13] M. J. S. Dewar, *J. Chem. Soc.* 2329 (1950).

[14] L. Orgel, T. L. Cottrell, W. Dick, and L. E. Sutton, *Trans. Faraday Soc.* **42,** 764 (1946).

[15] A. J. Owen, *Tetrahedron* **14,** 237 (1961).

[16] R. Pariser and R. G. Parr, *J. Chem. Phys.* **21,** 466 (1953).

[17] R. Pariser and R. G. Parr, *J. Chem. Phys.* **21,** 767 (1953).

[18] R. G. Parr and R. Pariser, *J. Chem. Phys.* **23,** 711 (1955).

[19] R. Pariser, *J. Chem. Phys.* **24,** 250 (1956).

CALCULATIONS

Because three different heteroatom Coulomb integrals in phenol blue are unknown, a three-factor composite design* was utilized which, by a regression treatment, permitted the responses to be fitted to an equation of the form:

$$R = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 \\ + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3. \quad (3)$$

The factor levels used are given in Table 1. The range of h_x values for each heteroatom was chosen to cover most of the values reported in the literature. For the calculations in Table 1, all resonance integrals were assumed to be equal to β_0, with the exception of the integral for the carbon-nitrogen single bond, which was set equal to $0{\cdot}8\beta_0$.[12]

TABLE 1. THREE-FACTOR COMPOSITE DESIGN FOR HMO CALCULATIONS ON PHENOL BLUE

Calc.	X_1	X_2	X_3	$h_{\dot{\dot{N}}}$[a]	$h_{\dot{N}}$[b]	h_O[c]
1	−1	−1	−1	0·80	0·28	0·61
2	1	−1	−1	1·70	0·28	0·61
3	−1	1	−1	0·80	0·82	0·61
4	1	1	−1	1·70	0·82	0·61
5	−1	−1	1	0·80	0·28	2·39
6	1	−1	1	1·70	0·28	2·39
7	−1	1	1	0·80	0·82	2·39
8	1	1	1	1·70	0·82	2·39
9	−1·68	0	0	0·50	0·55	1·50
10	1·68	0	0	2·00	0·55	1·50
11	0	−1·68	0	1·25	0·10	1·50
12	0	1·68	0	1·25	1·00	1·50
13	0	0	−1·68	1·25	0·55	0
14	0	0	1·68	1·25	0·55	3·00
15	0	0	0	1·25	0·55	1·50

[a] $h_{\dot{\dot{N}}} = 0{\cdot}45\ X_1 + 1{\cdot}25$. [b] $h_{\dot{N}} = 0{\cdot}27\ X_2 + 0{\cdot}55$. [c] $h_O = 0{\cdot}89\ X_3 + 1{\cdot}5$.

From the quadratic expression (3) a three-dimensional grid of 700 points (10 × 10 × 7) was generated for each response on an IBM 1620 Computer. Each response could then be examined throughout the entire factor space, and those regions thus determined which agreed with the experimental data.

The ASMO CI calculations on phenol blue were carried out, using as starting MO's those calculated with the HMO parameters of calculations 16 and 24 (Table 4). Bond lengths and angles had to be estimated. The nuclear co-ordinates used are given in Table 2. Although resonance integrals are usually evaluated empirically from spectroscopic data in this type of treatment, the large number of different integrals involved in a large molecule such as phenol blue required that these be estimated on

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TABLE 2. NUCLEAR COORDINATES FOR PHENOL BLUE[a]

Atom	x	y
1	0·000	4·130
2	0·000	2·900
3	1·264	2·110
3′	−1.264	2·110
4	1·264	0·790
4′	−1·264	0·790
5	0·000	0·000
6	0·000	−1·340
7	1·238	−2·055
8	2·442	−1·360
8′	1·238	−3·445
9	3·646	−2·055
9′	2·442	−4·140
10	3·646	−3·445
11	4·850	−4·140

[a] In angstrom units.

the basis of previously reported calculations. The values used are given in Table 3. Carbon-oxygen and carbon-nitrogen resonance integrals were calculated from the formula[20] $\beta_{pq} = A_{pq}/r^6$ with $A_{C\dot{N}} = -16{\cdot}3000$, $A_{C\ddot{N}} = -16{\cdot}0933$, and $A_{CO} = -9{\cdot}3226$. The A_{pq}-values were determined by fitting data for s-triazine,[17] pyrrole,[21] and formaldehyde[22] to the inverse sixth-power formula. Carbon-carbon resonance integrals were calculated from the formula $\beta_{CC} = -1779{\cdot}5 \exp(-4{\cdot}7862r)$. This equation fits the ethylene and benzene resonance integrals calculated by the semi-

TABLE 3. RESONANCE INTEGRALS FOR ASMO CI CALCULATIONS ON PHENOL BLUE

Bond	β(eV)
1, 2	−2·692
2, 3	−1·425
3, 4	−3·214
4, 5	−1·425
5, 6	−2·816
6, 7	−1·902
7, 8	−2·299
8, 9	−2·299
9, 10	−2·299
10, 11	−2·231

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[20] H. Kon, *Bull. Chem. Soc. Japan* **28**, 275 (1955).

[21] R. D. Brown and M. L. Heffernan, *Austr. J. Chem.* **12**, 319 (1959).

[22] R. D. Brown and M. L. Heffernan, *Trans. Faraday Soc.* **54**, 757 (1958).

empirical ASMO method with $(11/11)_{CC} = 11{\cdot}08$ eV.[23] Pariser and Parr[17] used a similar equation based upon $(11/11)_{CC} = 10{\cdot}53$ eV.

Penetration integrals were neglected in the calculations, the core Coulomb integrals being given by

$$\alpha_p = -I_p - \sum_{q \neq p} X_q \quad (qq/pp),$$

where I_p is an appropriate valence state ionization potential, X_q is the charge on core q, and (qq/pp) are bicentric Coulomb repulsion integrals. The last were calculated using the uniformly charged sphere approximation[16,17] for $r \geqslant 2{\cdot}80$ Å and the extrapolation formula of Pariser and Parr[17] for $r < 2{\cdot}80$ Å.

Interconfigurational matrix elements were calculated using the formulae given by Pariser.[19] In the configuration interaction treatment, all singly excited states within 7 eV of the ground state were included.

RESULTS AND DISCUSSION

1. *Interpretation of experimental data*

A molecular orbital treatment of phenol blue should be capable of explaining certain experimental observations. Among these are the following:

(a) Spectroscopic data[6–10] predict that the first excited state receives a larger contribution from Ib than does the ground state. Therefore, $\Delta q_0 > 0 > \Delta q_{\dot{N}}$ upon an $N \rightarrow V_1$ transition.

(b) The most plausible interpretation of the ground state dipole moment (5·80D[6]) is that Ib contributes to the resonance hybrid even in the ground state. This suggests that $1 < q_0 < 2$ and $1 < q_{\dot{N}} < 2$.

(c) The long-wavelength absorption maxima in solvent cyclohexane for some 3-substituted phenol blues are:[8] 3-Cl, 578 mμ; 3-H, 552mμ; 3-CH_3, 549 mμ; 3-OCH_3, 545 mμ. Substituents in the 4-, 8-, and 9-positions are considered later since steric effects are important at these positions. The consequences of the hypsochromic shift of the 3-methyl substituent relative to phenol blue will be examined first.

On neglecting second-order inductive effects, which are known to be small compared with other terms,[24] the change in the $N \rightarrow V_1$ transition energy of phenol blue as a result of the inductive effect of a 3-substituent is given approximately by Equation (4),[24]

$$(\Delta\Delta E)_{\text{inductive}} \cong (C_{b3}^2 - C_{a3}^2)\, d\alpha_3, \tag{4}$$

where C_{a3} and C_{b3} denote the atomic orbital coefficients of atom 3 in the *a*th and *b*th molecular orbital, *a* and *b* refer to the highest occupied and lowest unoccupied MO's of phenol blue, respectively, and $d\alpha_3$ is the change in the Coulomb integral of atom 3

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[23] Formulae for the energies of the N and V_1 states of ethylene are given by R. G. Parr and B. L. Crawford, Jr., *J. Chem. Phys.* **16**, 526 (1948). With the zero differential overlap approximation, the $N \rightarrow V_1$ transition energy is, in the notation of Pariser and Parr,[16] $K_{12} + (4\beta^2 + K_{12}^2)^{\frac{1}{2}}$. The experimental $N \rightarrow V_1$ interval is 7·6 eV. Assuming $(11/11)_{CC} = 11{\cdot}08$ eV[16] and using the extrapolation formula given by Pariser and Parr (Ref. 17, Eqn 13) for determining $(11/22)_{CC}$, one calculates $\beta = -2{\cdot}784$ eV ($r = 1{\cdot}35$ Å). The ${}^1A_{1g} \rightarrow {}^1B_{2u}$ transition energy in benzene is 4·71 eV (experimental) or $-2\beta + 1/6[(11/22) - 3(11/33) + 2(11/44)]$ (theoretical).[19] Using the same method of calculating electron/repulsion integrals, one calculates $\beta = -2{\cdot}299$ eV ($r = 1{\cdot}39$ Å).

[24] H. C. Longuet-Higgins and R. G. Sowden, *J. Chem. Soc.* 1404 (1952).

as a result of the inductive effect of the substituent. By taking $d\alpha_3$ as $-0{\cdot}1\beta_0$ for methyl,[24] then a hypsochromic shift is predicted if $C_{b3} > C_{a3}$, and a bathochromic shift, if $C_{b3} < C_{a3}$ by the inductive effect alone.

The hyperconjugative effect of the methyl group is given by Equation (5),[24]

$$(\Delta\Delta E)_{\text{hyperconjugation}} \cong \beta_{3s}^{\;2}\left[C^2\left(\frac{C_{1s}^{\;2}}{E_b - E_1} + \frac{C_{2s}^{\;2}}{E_b - E_2}\right) - C_{a3}^{\;2}\left(\frac{C_{1s}^{\;2}}{E_a - E_1} + \frac{C_{2s}^{\;2}}{E_a - E_2}\right)\right], \qquad (5)$$

where β_{3s} is the resonance integral of the C—C bond between position 3 of phenol blue and the methyl carbon atom; E_1 and E_2 are the energies of the two MO's, Ψ_1 and Ψ_2, of a hypothetical isolated methyl group where $E_1 < E_2$; and C_{1s} and C_{2s} are the atomic orbital coefficients for the carbon atom in Ψ_1 and Ψ_2. Longuet-Higgins and Sowden[24] showed that if

$$E_1 < E_a < 0 < E_b < E_2,$$

then the hyperconjugative effect will always be bathochromic, regardless of the relative magnitudes of C_{a3} and C_{b3}. In phenol blue, however, the order

$$E_1 < E_a < E_b < 0 < E_2$$

is often observed, the particular order depending upon the choice of Coulomb and resonance integrals. If it is assumed that $E_1 = -E_2$,[25] it may be shown in this case that $(\Delta\Delta E)$ hyperconjugation < 0 if $C_{b3} < C_{a3}$, but if $C_{b3} > C_{a3}$, then a hypsochromic or bathochromic shift may result, depending upon the relative magnitudes of C_{a3}, C_{b3}, E_a, and E_b.

In summary, for methyl substitution:

$E_1 < E_a < 0 < E_b < E_2$
$C_{b3} > C_{a3}$
Inductive — hypsochromic
Hyperconjugative — bathochromic
$C_{b3} < C_{a3}$
Inductive — bathochromic
Hyperconjugative — bathochromic
$E_1 < E_a < E_b < 0 < E_2$
$C_{b3} > C_{a3}$
Inductive — hypsochromic
Hyperconjugative — bathochromic or hypsochromic
$C_{b3} < C_{a3}$
Inductive — bathochromic
Hyperconjugative — bathochromic

Thus the experimental fact that a 3-methyl group hypsochromically shifts the absorption maximum of phenol blue requires $C_{b3} > C_{a3}$.

The question remains: Is such a model (i.e., $C_{b3} > C_{a3}$) compatible with a bathochromic effect of 3-Cl and a hypsochromic effect of 3-OCH$_3$ relative to phenol blue? Both substituents are inductively electron-withdrawing, and both are capable of

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[25] The validity of this assumption for determining the sign of $\Delta\Delta E$ is discussed in Ref. 24.

donating two p-electrons to the π-electronic system. By Eqn 4 the inductive effect of both substituents would be bathochromic, and the question may therefore be rephrased: Can the conjugative effect of these substituents be hypsochromic?

Equation (5) for a methyl substituent may be rewritten for monatomic substituents[26] in the form[27]

$$(\Delta\Delta E)_{\text{conjugation}} \cong \beta_{3s}{}^2 \left[C_{b3}{}^2 \left(\frac{1}{E_b - \alpha_s} \right) - C_{a3}{}^2 \left(\frac{1}{E_a - \alpha_s} \right) \right]. \tag{6}$$

where α_s is the Coulomb integral of the heteroatom. For substituents like Cl, OCH_3, and NH_2, it will generally be true that $\alpha_s < E_a < E_b$, in which case

$$0 < \left(\frac{1}{E_b - \alpha_s} \right) < \left(\frac{1}{E_a - \alpha_s} \right).$$

The conjugative effect of the substituent may then be bathochromic or hypsochromic, depending upon the relative magnitudes of the C's, E's, and α_s. Thus the observed substituent effects could be accommodated by the aforementioned model.

2. *Correlation of MO calculations with experimental data*

The results of the initial calculations on phenol blue, using parameters given in the literature, are presented in Table 4 (Numbers 16–18). With these parameters condition (b) is fulfilled, but conditions (a) and (c) are not satisfied. It has been found that almost any rational choice of Coulomb integrals will predict $\Delta q_{\dot{N}} < 0$ upon an $N \rightarrow V_1$ transition, but the sign of Δq_0 is erratic and cannot be predicted with certainty.

TABLE 4. RESULTS OF HMO CALCULATIONS ON PHENOL BLUE[a]

Calc.	$h_{\ddot{N}}$	$h_{\dot{N}}$	h_O	$q_{\ddot{N}}$	$q_{\dot{N}}$	q_O	$\Delta q_{\ddot{N}}$	$\Delta q_{\dot{N}}$	Δq_O	Δq_s[b]
16[c]	1·50	0·50	1·00	1·884	0·983	1·633	−0·026	0·295	−0·119	−0·028
17[d]	1·00	0·50	1·00	1·730	1·063	1·505	−0·129	0·267	−0·047	−0·047
18[e]	2·00	1·00	2·00	1·918	1·231	1·533	−0·057	0·203	0·001	−0·033
19	1·00	0·23	2·80	1·879	0·751	1·855	−0·319	0·381	0·002	−0·025
20	0·80	0·23	3·00	1·757	0·770	1·913	−0·377	0·354	0·003	−0·017
21	0·60	0·10	3·00	1·674	0·730	1·931	−0·422	0·336	0·004	−0·010
22	1·34	0·55	0·60	1·883	1·125	1·371	−0·067	0·176	−0·068	−0·045
23	0·62	0·50	0·61	1·714	1·099	1·452	−0·289	0·275	−0·012	−0·024
24	1·34	1·00	0·50	1·892	1·441	1·109	−0·113	0·053	0·152	0·046

[a] All responses in this table were obtained by solution of the secular determinant.

[b] Change in electron density upon an $N \rightarrow V_1$ transition at the carbon atom *ortho* to the carbonyl.

[c] Parameters from Ref. 12.

[d] Parameters from Ref. 13.

[e] Parameters from Ref. 15.

The regression coefficients for fitting responses of phenol blue to parameter values according to Eqn 3 are given in Table 5. In the last column are given the multiple correlation coefficients (MCC), the squares of which give the fraction of the

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[26] Monatomic substituents are those contributing one p-orbital to the π-electronic system; cf. Ref. 27.

[27] D. Peters, *J. Chem. Soc.* 1993 (1957).

TABLE 5. REGRESSION COEFFICIENTS FOR FITTING RESPONSES OF PHENOL BLUE TO EQN 3

Response	b_0	b_1	b_2	b_3	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}	MCC[a]
$q_O{}^b$	1·7858	−0·0425	−0·0396	0·2650	−0·0166	−0·0048	−0·1649	−0·0320	−0·0301	0·0150	0·9848
$q_{\dot{N}}{}^b$	0·9489	−0·0329	0·1775	−0·0998	0·0118	0·0142	0·0671	0·0008	−0·0118	0·0027	0·9801
$q_{\ddot{N}}{}^b$	1·8453	0·1456	−0·0165	−0·0093	−0·0067	−0·0013	0·0159	0·0334	0·0500	0·0021	0·9460
$\Delta q_O{}^c$	−0·0297	−0·0183	0·0298	−0·0183	−0·0132	−0·0106	0·0436	0·0104	0·0136	−0·0448	0·8110
$\Delta q_{\dot{N}}{}^c$	0·3465	0·0126	−0·0511	0·0913	−0·0180	0·0010	−0·0702	0·0027	0·0438	0·0045	0·9525
$\Delta q_{\ddot{N}}{}^c$	−0·1572	0·0848	0·0063	−0·0351	−0·0020	−0·0065	0·0057	−0·0139	0·0012	0·0268	0·9665
$\Delta q_2{}^d$	−0·0367	−0·0103	0·0115	−0·0126	−0·0013	−0·0007	0·0196	0·0046	−0·0023	−0·0144	0·9291
ΔE^e	−0·5633	−0·0715	0·0804	−0·0267	0·0308	0·0016	0·0068	0·0001	−0·0205	0·0193	0·9833

[a] Multiple correlation coefficient.

[b] Electron density in ground state.

[c] Change in electron density upon an $N \rightarrow V_1$ transition.

[d] Change in electron density upon an $N \rightarrow V_1$ transition at the carbon *ortho* to the carbonyl.

[e] HMO transition energy for the $N \rightarrow V_1$ transition.

variability that is accounted for by the model (i.e., the quadratic equation). Clearly the change in electron density on oxygen, Δq_0, shows the poorest correlation, indicating that higher-order terms would have to be considered to improve the fit.

Examination of response surfaces generated using Eqn 3 with appropriate coefficients, revealed only two regions in which conditions (a)–(c) were apparently satisfied (Fig. 1). Region I was characterized by $h_{\dot{N}} < h_{\ddot{N}} < h_0$,* the minimum and maximum values for these parameters being approximately: $h_{\dot{N}} = 0{\cdot}10–0{\cdot}71$; $h_{\ddot{N}} = 0{\cdot}50–1{\cdot}25$; $h_0 = 2{\cdot}57–3{\cdot}00$. In Region II, $h_{\dot{N}} < h_{\ddot{N}}$, but h_0 can assume values less than or slightly greater than $h_{\dot{N}}$. By far the largest portion of the region is characterized by $h_0 < h_{\dot{N}} < h_{\ddot{N}}$. The minimum and maximum parameter values in this region are approximately: $h_{\dot{N}} = 0{\cdot}39–1{\cdot}04$; $h_{\ddot{N}} = 0{\cdot}44–2{\cdot}00$; $h_0 = 0–1{\cdot}06$.

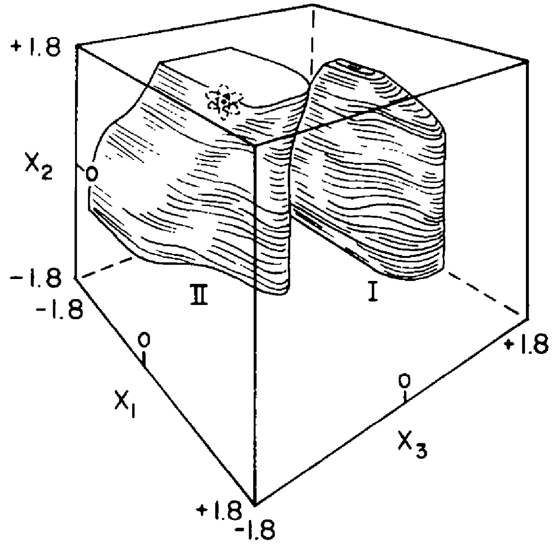

FIG. 1. Shaded areas show regions in which conditions (a)–(c) are apparently satisfied. Solid dot shows location of parameters chosen for calculation of substituent effects.

Solution of the secular determinant for several sets of parameters in Region I showed that actually $\Delta q_3 < 0$. (Table 4, calculations 19–21). Apparently a maximum is reached in this region at $\Delta q_3 \simeq -0{\cdot}01$. Solution of the secular determinant for selected parameter values in Region II with $h_{\dot{N}} < h_0 < h_{\ddot{N}}$ gave $\Delta q_0 < 0$ and $\Delta q_3 < 0$ (calculations 22 and 23). To bring these responses into line with conditions (a)–(c), it was found necessary to decrease h_0. The parameter values within the experimental design which have been found to satisfy these conditions have $h_0 < h_{\dot{N}}$. A set of parameters which gives agreement with conditions (a)–(c) are: $h_0 = 0{\cdot}50$; $h_{\dot{N}} = 1{\cdot}00$; $h_{\ddot{N}} = 1{\cdot}34$ (Table 4, calculation 24). These values are not unique.

The order $h_0 < h_{\dot{N}}$ is the reverse of that usually used for these atoms,[12] indicating an electronegativity reversal. The calculated electron density on oxygen is considerably lower than that calculated using literature h- and k-parameters values (calculations 16–18). It has been proposed that Coulomb integrals should actually be a

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* Regions I and II contained volume elements satisfying conditions (a)–(c), for which $h_{\dot{N}} > h_{\ddot{N}}$, but this order was considered too unlikely to warrant further consideration of these volume elements.

TABLE 6. PARAMETERS FOR CALCULATING SUBSTITUENT EFFECTS IN PHENOL BLUE[a]

Substituent	Electronegativity parameter	Bond integral
CH_3O	$h_O = 2{\cdot}0$	$k_{C-O} = 0{\cdot}8$
F	$h_F = 3{\cdot}0$	$k_{C-F} = 0{\cdot}7$
Cl	$h_{Cl} = 2{\cdot}0$	$k_{C-Cl} = 0{\cdot}4$
Br	$h_{Br} = 1{\cdot}5$	$k_{C-Br} = 0{\cdot}3$
Methyl[b]: $C\alpha—C_\beta{\equiv}H_3$	$h_{C\alpha} = -0{\cdot}1$	$k_{C-C} = 0{\cdot}7$
	$h_{H_3} = -0{\cdot}2$	$k_{C\equiv H_3} = 2{\cdot}0$
AIP[c]	$0.1h_X$	

[a] All values except methyl taken from Ref. 12. [b] Values from Ref. 24.
[c] Auxiliary inductive parameter for heteroatom substituents.

TABLE 7. $N \rightarrow V_1$ CHANGE IN PHENOL DYES[a]

Substituent	$\lambda_{max}(m\mu)$[b]	$\Delta\Delta E(\text{calc.})/\beta_O$
3-Br	579[c]	+0·0050
3-Cl	578[c]	0.0064
Unsubstituted	552[c]	—
$3\text{-}CH_3$	549[c]	−0.0034
$3\text{-}OCH_3$	545[c]	−0.0018
$4\text{-}OCH_3$	543[c]	−0.0023
8-Cl[d]	560	−0.0018
8-F[d]	553	−0.0016
$N \rightarrow V_1$ CHANGE IN NAPHTHOL DYES[a,e]		
16-Cl	598[f]	+0.0028
$16\text{-}OCH_3$	588[f]	−0.0014
$14\text{-}OCH_3$	587[f]	−0.0001
13,16-Cl	587[f]	+0.0047
Unsubstituted	582[f]	—
$14\text{-}CH_3$	581[f]	−0.0008
$14,15\text{-}OCH_3$	577[f]	−0.0015
$15\text{-}OCH_3$	576[f]	−0.0014
$16\text{-}NH_2$	574[f]	−0.0031
$13\text{-}OCH_3$	570[f]	−0.0019
$15\text{-}NH_2$	566[f]	−0.0035
$13,16\text{-}OCH_3\text{-}14\text{-}CH_3$	556[f]	−0.0041
$13,16\text{-}OCH_3$	554[f]	−0.0033

[a] Using parameters for calculation (24) and those in Table 4.
[b] In cyclohexane. [c] Ref. 8. [d] These substituents refer to the dye formed from α-naphthol and the halo-substituted *p*-amino-diethylaniline. The unsubstituted naphthol dye has λ_{max} (C_6H_{12}) 564 mμ (Ref. 33). [e] For numbering system, see Table 8. [f] Ref. 10.

function of charge density.[28-31] It is probable that application of an ω-technique[29-31] to calculations 16–18 would accomplish a result similar to the regression treatment. However ω-values for heteroatoms have not been established.

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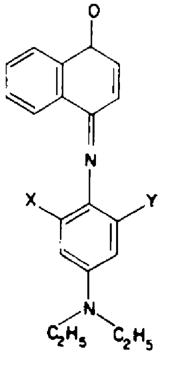
[28] G. W. Wheland and D. E. Mann, *J. Chem. Phys.* **17**, 264 (1949).
[29] A. Streitwieser, Jr., *J. Amer. Chem. Soc.* **82**, 4123 (1960).
[30] A. Streitwieser, Jr., and P. M. Nair, *Tetrahedron* **5**, 149 (1959).
[31] Ref. 1, pages 115–116.

That condition (c) is satisfied was determined by substitution of appropriate parameter values (Table 6) into Eqs. 4, 5 and 6 with the following terms: $E_a = \alpha + 0{\cdot}538\beta$; $E_b = \alpha + 0{\cdot}085\beta$; $C_{a3}{}^2 = 0{\cdot}0414$; $C_{b3}{}^2 = 0{\cdot}0871$. The results (Table 7) agree qualitatively with the experimental data, predicting a bathochromic shift for bromo- and chloro-substituents and a hypsochromic shift for methyl and methoxyl.

With regard to substituents in the 4- and 8-positions, i.e., *ortho* to the azomethine bridge, steric effects must be considered. Vittum and Brown[32] showed that the $N \rightarrow V_1$ absorption maximum of phenol blue is bathochromically shifted by 4,4'-dimethyl substitution. Other examples are known which suggest that this is a general phenomenon. For example, the long-wavelength absorption maximum in cyclohexane of the naphthol dyes IIa–IIe increases with increasing steric hindrance to planarity.[33]



		λ_{max}
II a.	X = H; Y = H	564 mμ
b.	X = H; Y = C_2H_5	581
c.	X = H; Y = n-C_3H_7	584
d.	X = H; Y = t-C_4H_9	597
e.	X = CH_3; Y = CH_3	618

To be certain of the electronic effect of a 4- or 8-substituent in phenol blue, consideration was given only to hypsochromically shifted dyes. Again, qualitative agreement of the calculated shifts was obtained (Table 7) for the few examples known of this type which contain monatomic substituents.

The parameters for calculation (24) and those in Table 6 were also applied to naphthol dyes, with the results given in Table 7. For the disubstituted dyes, an additive relationship was assumed.[24] The direction of the shift is qualitatively predicted for ten of the twelve substituted dyes.

In Table 8 are presented the complete electron-density data for phenol blue and its naphthol analog in the ground and the first excited states, using the parameters of calculation (24).

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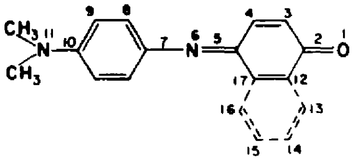
[32] P. W. Vittum and G. H. Brown, *J. Amer. Chem. Soc.* **69**, 152 (1947).

[33] R. L. Bent, G. H. Brown, D. P. Harnish, J. R. Thirtle, and L. K. J. Tong, Eastman Kodak Co., unpublished data.

TABLE 8. ELECTRON DENSITIES[a] (HMO CALCULATION)



Atom	Phenol blue		Naphthol dye	
	N	V_1	N	V_1
1	−0·109	−0·261	−0·187	−0·336
2	+0·115	+0·060	+0·135	+0·070
3	+0·068	+0·022	+0·088	+0·021
4	+0·017	−0·012	+0·030	−0·014
5	+0·173	+0·093	+0·201	+0·104
6	−0·441	−0·494	−0·458	−0·499
7	+0·007	+0·130	0·000	+0·137
8	+0·001	+0·026	−0·004	+0·025
9	−0·044	+0·010	−0·046	+0·014
10	+0·061	+0·158	+0·053	+0·162
11	+0·108	+0·221	+0·102	+0·229
12			+0·010	−0·007
13			+0·034	+0·018
14			+0·031	+0·016
15			+0·017	+0·003
16			+0·048	+0·027
17			0·005	−0·012

[a] Figures given are net charges in units of e.

The results of the ASMO CI calculations on phenol blue are given in Table 9 and Fig. 2. For purposes of comparing calculations I (starting MO's those of calculation (16)) and II (starting MO's those of calculation (24)), the energies of the two ground-state configurations were calculated from the formula[16]

$$E\chi_0 = \sum_i I_i + \tfrac{1}{2} \sum_{ij} (J_{ij} - K_{ij}'),$$

in which the summations are over the occupied molecular spin-orbitals, and the notation and definition of terms are the same as those of Pariser and Parr.[16] Once this relationship was established, the energies of the ground (E) and first excited (V_1) *states* resulting from the configuration interaction treatment could then be compared. The results are given below and in Fig. 2.

$$E\chi_0\,(\text{I}) - E\chi_0\,(\text{II}) = -0{\cdot}217\ \text{ev.}$$
$$E_N\,(\text{I}) - E_N\,(\text{II}) = -0{\cdot}089\ \text{ev.}$$
$$E_{V1}\,(\text{I}) - E_{V1}\,(\text{II}) = +0{\cdot}190\ \text{ev.}$$

It is seen that, on an energy-level basis, the two calculations give almost identical results after configuration interaction. The $N \rightarrow V_1$ spectroscopic interval is in both cases ~5 eV, which is ~3 eV higher than the experimental value (2·25 eV). The lack of agreement with experiment is in large part probably caused by (a) incorrect resonance integrals, and (b) insufficient configuration interaction of the 48 singly excited

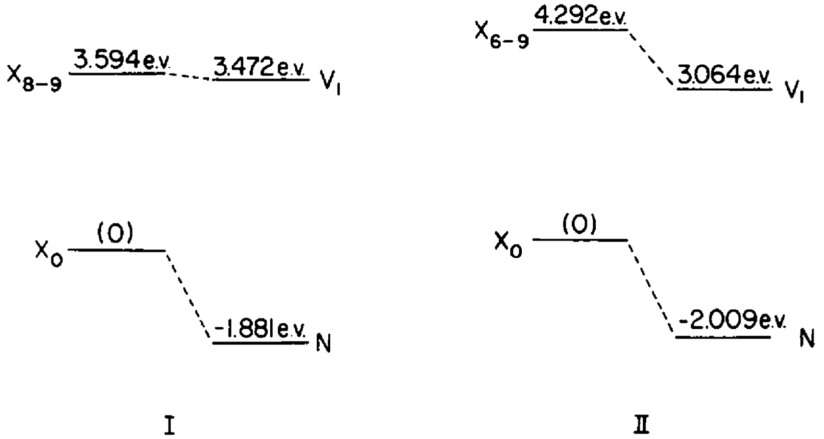


FIG. 2. Energy levels of phenol blue calculated by the ASMO CI method. (I) Using parameters of calculation 16 for starting MO's; (II) Using parameters of calculation 24 for starting MO's. Dotted lines show energy level lowering as a result of configuration interaction.

TABLE 9. CONFIGURATIONAL WAVE FUNCTIONS FOR PHENOL BLUE

Configuration	Coefficients			
	N^a	V_1^a	N^b	V_1^b
χ_0	0·8752	−0·1666	0·8911	−0·1104
$\chi_{6\to 9}$	−0·0006	0·0212	0·0001	0·0270
$\chi_{8\to 9}$	0·3883	0·7076	−0·0603	0·8569
$\chi_{5\to 9}$	0·0008	0·0036	−0·0001	−0·0159
$\chi_{7\to 9}$	−0·0412	−0·1733	0·3555	0·1396
$\chi_{4\to 9}$	−0·1200	−0·0097	−0·1917	−0·4390
$\chi_{8\to 12}$	−0·1742	0·6337	−0·0730	0·0880
$\chi_{8\to 11}$	−0·0088	−0·0645	−0·0104	−0·0040
$\chi_{8\to 10}$	0·0066	0·0925	0·0083	0·0422
$\chi_{8\to 13}$	0·1414	−0·1571	0·1562	0·0673
$\chi_{3\to 9}$	c	c	0·0885	0·1550
$\chi_{1\to 9}$	c	c	−0·0385	0·0484
$\chi_{7\to 12}$	0·1295	−0·0450	c	c

[a] Using parameters of calculation (16) for starting MO's.
[b] Using parameters of calculation (24) for starting MO's.
[c] Not included in configuration interaction treatment, as configuration is more than 7 ev. above χ_0.

configurations (all singlets), only 10 (calc. I) and 11 (calc. II) of which were included in the configuration interaction treatment.

On the other hand, the configurational wave functions (Table 9) show that, to the extent that configuration interaction has been carried out, the HMO parameters of calculation (24) probably come closer to representing the electron densities correctly than do those of calculation (16). This is particularly evident in the V_1 state, where the $\chi_{8\to 9}$ configuration contributes 73 percent to the electron-density pattern in calculation II, but only 50 percent in calculation I.

TABLE 10. ELECTRON DENSITIES IN PHENOL BLUE[a,b] (ASMO CI METHOD)

Atom	N^c	V_1^c	N^d	V_1^d
1	−0·599	−0·479	−0·138	−0·275
2	0·168	0·123	0·108	0·081
3	−0·011	0·037	0·055	0·017
4	0·069	0·022	0·021	−0·007
5	0·063	0·074	0·158	0·113
6	−0·028	−0·121	−0·443	−0·503
7	0·015	0·009	0·018	0·120
8	0·043	0·023	0·002	0·032
9	−0·030	−0·013	−0·033	0·000
10	0·107	0·079	0·063	0·130
11	0·130	0·177	0·145	0·252

[a] Figures given are net charges in units of *e*.
[b] For numbering, see Table 8.
[c] Calculation I.
[d] Calculation II.

The calculated electron densities for the two Pariser-Parr calculations are given in Table 10. Even with the inclusion of all singly excited states within 7 eV of the ground states, the results are still largely determined by the choice of starting MO's. Although it would be of interest to include all 48 singly excited states, it is questionable whether this would be worthwhile in view of the uncertainties in the geometry of the molecule and the resonance integrals. Further, it has been shown[34] that the energies of some two-electron states may be comparable to the one-electron state and these should then be included in a configuration interaction treatment.

Based upon the results just given, it is evident that heteroatom parameters which are suitable for one type of molecule should not be carried over *a priori* to other types. This *can* be a dangerous extrapolation, although in many cases it has been known to work. It is possible that, in some cases where this has been done successfully, the experimenter may have been dealing with rather "flat" response surfaces, in which case the results would not be readily affected by the choice of parameters. On the other hand, if one were working on a "ridge" or a "peak," then a slight change in parameters could have a large effect upon the results. Particularly when one is starting calculations on a new class of compounds, a knowledge of response surfaces may be well worth the added labor of the necessary molecular-orbital calculations and regression treatment.

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[34] D. P. Craig, *Proc. Roy. Soc.* **A200**, 474 (1950).