Comparison of Omega and PPP Techniques for Reactivity Calculations in Methyl-Substituted Naphthalenes

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The dependence of electron density, superdelocalizability and localization energy on the value of the parameter for the inductive effect of the methyl group in 1,4-dimethyl naphthalene is exactly the same when calculated by the Omega or by the Pople-Pariser-Parr techniques.

Die Abhängigkeit der Elektronendichte, der Superdelokalisierbarkeit und der Lokalisierungs-energie vom Wert des Parameters für den induktiven Effekt der Methylgruppe in 1,4-Dimethyl-naphthalin ist genau dieselbe, wenn man diese Größen mit der Omegatechnik oder der PPP-Methode berechnet.

La densité électronique, la super délocalisabilité et l'énergie de localisation du 1,4 diméthyl naphtalène dépendent de la même manière de la valeur du paramètre de l'effet inductif du groupe méthyle selon que les calculs sont effectués par la méthode oméga ou par la méthode de Pople-Pariser-Parr.

Introduction

The present note represents a comparison of computational techniques carried out preliminary to extensive calculations on the electrophilic reactivity of methyl-substituted naphthalenes[1]. Calculations on such systems require a suitable model for the methyl group; once the model is chosen, a choice of parameters must be made, and the calculated results then depend, in principle, on both the model and the numerical values of the parameters. The objective of this work is to investigate how the common reactivity indices, as calculated by the Omega and the Pople-Pariser-Parr (PPP) techniques, depend on the numerical value of the parameter for the inductive effect of the methyl group. A subsidiary interest of such a comparison is practical: inasmuch as the PPP technique requires non-trivial amounts of computer time, it is useful to know whether the simpler omega technique does not yield similar results more cheaply.

Large number of preliminary results have shown that in general, regardless of models and numerical values of parameters, virtually all calculated reactivity indices give the correct most reactive position whenever electrophilic substitution in a methyl-naphthalene takes place at an alpha position, but mostly fail when substitution takes place at a beta position. We will therefore concentrate on the

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[1] For a preliminary report, see P. Canonne, Le-Khac Huy, and W. Forst, paper presented before the Division of Organic Chemistry, 156th National Meeting of the American Chemical Society, Atlantic City, N. J. September 1968.

latter case, of which the 1,4-dimethyl naphthalene[2] is a typical example. Experimental results obtained by Dallinga *et al.* [1] on the hydrogen-deuterium exchange give the order of reactive positions as $3 > 5 > 6$, the respective rate constants being $\log k_3 = 2.51$, $\log k_5 = 1.48$, $\log k_6 = 0.73$, in units of hours$^{-1} \times 10^3$.

Method of Calculation

a) Omega Technique

As originally conceived [2], the technique approximates π-electron interaction by assuming a linear relationship between the Coulomb integral α and charge density q:

$$\alpha_r^{t+1} = \alpha + \omega \beta (1 - q_r^t) . \tag{1}$$

We have also introduced a dependence of the exchange integral β_{rs} on bond length (cf. also Nounou [3]) using a relation due to Longuet-Higgins and Salem [4]:

$$\beta_{rs}^{t+1} = \beta \exp\left[-2.683 (0.12 - 0.18 \, p_{rs}^t) \right] . \tag{2}$$

Here α is the standard Coulomb integral, β is the standard exchange integral corresponding to bond length of 1.39 Å, and p_{rs} is the mobile bond order between carbon atoms r and s. The Coulomb integral of atom r is changed if the π-electron density q_r, obtained by the solution of the Hückel determinant, is different from unity. Similarly β_{rs} is changed as a function of the Hückel p_{rs}. Charge redistribution is accomplished by successive iterations (superscript $t =$ number of iterations) which are continued until self-consistency in both q_r and β_{rs} is attained. The criterion of self-consistency was taken as a difference of less than 10^{-4} in all q_r's and β_{rs}'s between two successive iterations. Overlap is neglected.

To avoid convergence problems, and to reduce the number of iterations, a modification of the ω-technique due to Ettinger [5] was used, which consists of taking the average charge densities of two preceding interations as the input for the next iteration. Hence q_r^t in Eq. (1), i.e. the input for the $(t+1)$st iteration, is replaced by $(q_r^t + q_r^{t-1})/2$. The usual values of ω are between 1 and 2; we have used Streitwieser's [2] value $\omega = 1.4$. Calculations were accomplished by means of our own program written in Fortran IV, but essentially a similar program is available from the Quantum Chemistry Program Exchange as QCPE 110.
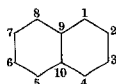
b) Pople-Pariser-Parr Technique

We have used a standard version of the technique [6], in which equations analogous to (1) and (2) become

$$\alpha_r = (\alpha_r)_{\text{core}} + \tfrac{1}{2} q_r \gamma_{rr} + \sum_{s \neq r} (q_s - 1) \gamma_{rs} , \tag{3}$$

$$\beta_{rs} = (\beta_{rs})_{\text{core}} - \tfrac{1}{2} p_{rs} \gamma_{rs} . \tag{4}$$

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[2] The following numbering is used:

γ_{rr} and γ_{rs} are the one- and two-center two-electron repulsion integrals, respectively, and the other symbols have their usual significance. The parameter values used were $I_C = 11.16$ eV [7], $\beta_{CC}(1.39$ Å$) = 2.39$ eV [6]; all angles were assumed to be 120°. The integrals γ_{rs} were calculated from a formula due to Roothaan [8], using for the electron affinity of the carbon atom the value $E_C = 0.03$ eV [7]. The criterion of self-consistency was a variation of less than 10^{-4} in wave function coefficients of occupied orbitals. Calculations were done by means of a program in Fortran IV, kindly furnished by Dr. S. Fraga (University of Alberta), suitably modified for our purpose.

Model for Methyl Group

We have chosen for simplicity the inductive model, which assumes that the only effect of the methyl group is to make the adjacent ring carbon atom more electro-positive (i.e. to reduce its effective nuclear charge), without any actual transfer of charge between the ring and the methyl group.

In the ω-technique, a reduction of effective nuclear charge is accomplished by modifying Eq. (1): when index r refers to the carbon atom adjacent to the methyl group, α in Eq. (1) is replaced by

$$\alpha + h\beta,$$

where h is a negative parameter for the inductive effect of the methyl group. In the PPP technique, Eq. (3) is similarly modified by decreasing $(\alpha_r)_{core}$ and γ_{rr} for the adjacent carbon. I_C and γ_{rr} then become $I_C - H$ and $\gamma_{rr} - H$, respectively, where H (eV) is positive; H is thus the PPP equivalent of the inductive parameter h. By division with $\beta = 2.39$ eV, H can be expressed in units of β to make it directly comparable with h.

Reactivity Indices

Three reactivity indices were chosen as reasonably applicable to an electrophilic substitution: electron density q_r, superdelocalizability S_r and localization energy L_r. Superscripts ω and P are used to distinguish indices calculated by the omega and PPP techniques.

If c_{jr} is the wave function coefficient of atom r in orbital j, the total π-electron density at atom r is

$$q_r = 2 \sum_{j=1}^{m} c_{jr}^2 \quad \text{(sum over occupied orbitals)}$$

The mobile bond order between atoms r and s (cf. Eqs. (2) and (4)) is defined as

$$p_{rs} = 2 \sum_{j=1}^{m} c_{jr} c_{js}.$$

Superdelocalizability for an electrophilic substitution is defined as

$$S_r = 2 \sum_{j=1}^{m} \frac{c_{jr}^2}{\varepsilon_j}$$

where ε_j is the one-electron energy in orbital j.

As usual, we define localization energy in electrophilic substitution as the difference in π-energy between the original molecule and a "residual molecule" in which two electrons and one carbon atom at position r of attack are taken out of conjugation. However in contrast to some previous treatments, we have applied iterations to both the original reactant molecule and the "residual molecule", and in the latter have carried out all computations to self-consistency at each reactive position r separately. The localization energy so obtained we call L_r^ω and L_r^P, respectively. In the PPP treatment, the integrals γ_{rs} were taken to be the same in both the original molecule and in the "residual molecule".

Flurry and Lykos [9] have assumed that the inductive effect of the methyl group also effects the two-center integrals γ_{rs} involving a methyl-substituted center. Because of the uncertainty how such a γ_{rs} should be modified further in the "residual molecule", we have neglected this effect.

Results and Discussion

The results of the calculations are shown in Figs. 1–3. The virtually linear dependence of all three reactivity indices on h or H is particularly interesting. Although the ω- and the PPP-techniques are related in the sense that both are approximations to a true self-consistent treatment, and therefore should yield similar results, it is nevertheless quite striking to see in these three Figures that both techniques yield not only the same order of reactive positions, but also substantially the same dependence on the inductive parameters h or H. Particularly noteworthy is the reversal of reactivity order at positions 5 and 2 for superdelo-
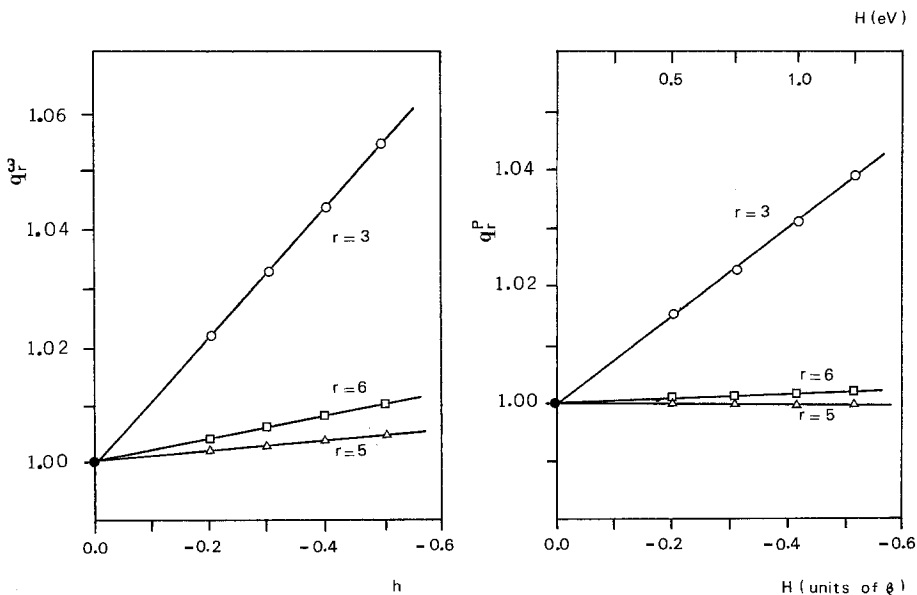

Fig. 1. Electron density of 1,4-dimethyl naphthalene (open symbols) at position r, calculated by the omega technique (q_r^ω) and by the PPP technique (q_r^P) as a function of inductive parameter h and H. Full circle refers to naphthalene
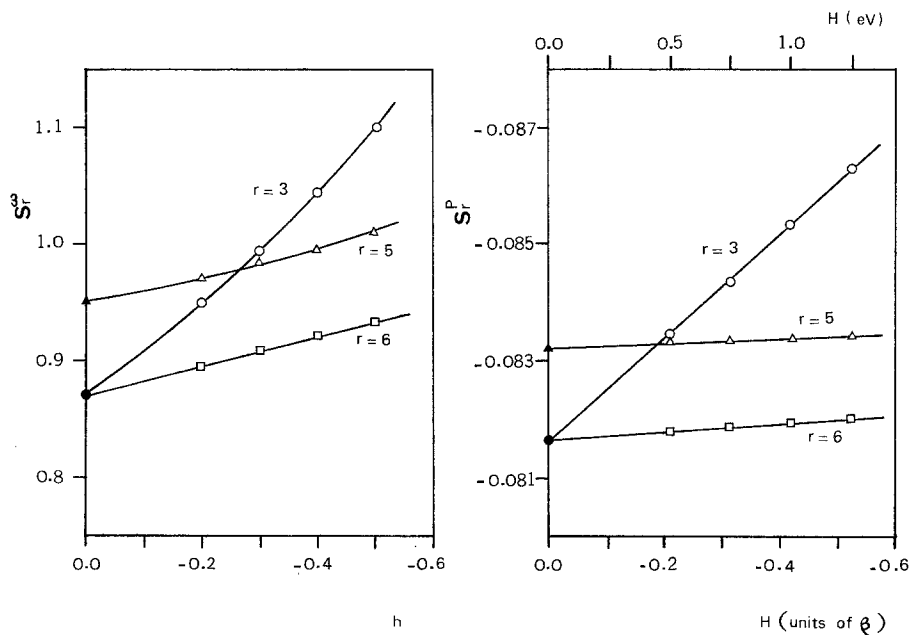
Fig. 2. Superdelocalizability of 1,4-dimethyl naphthalene (open symbols) at position r, calculated by the omega technique (S_r^ω) and by the PPP technique (S_r^P), as a function of inductive parameter h and H. Full triangle and circle represent alpha and beta positions, respectively, in naphthalene
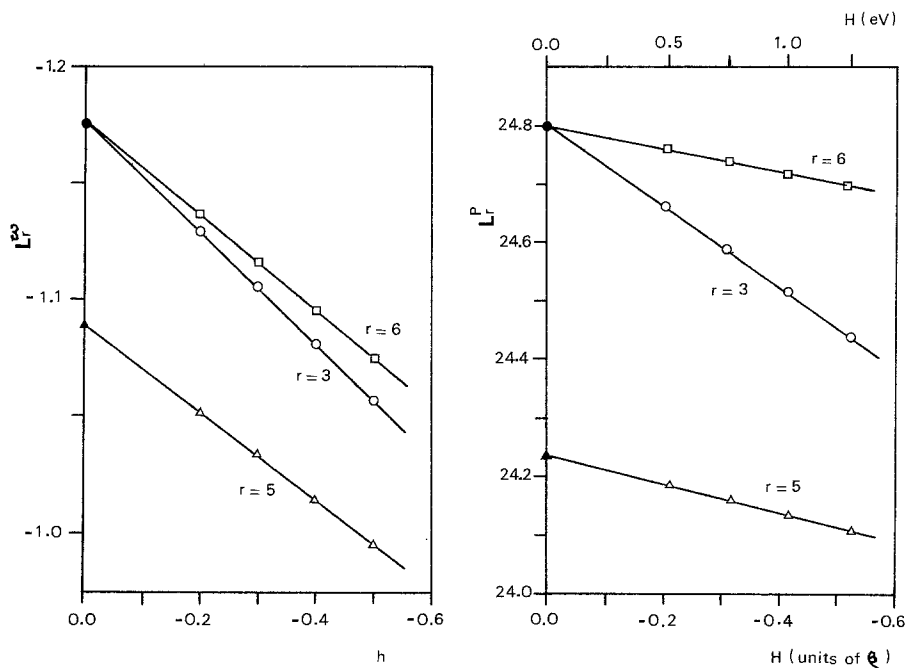

Fig. 3. Localization energy of 1,4-dimethyl naphthalene (open symbols) at position r, calculated by the omega technique (L_r^ω) and by the PPP technique (L_r^P), as a function of inductive parameter h and H. Full triangle and circle represent alpha and beta positions, respectively, in naphthalene

calizability S_r, which occurs at practically the same value of the inductive parameter in both techniques. It is a perfect illustration of the perils attendant to drawing conclusions about order of reactive positions from just one value of an adjustable parameter.

From the change in ionization potential of the methyl radical on successive methyl substitution, Flurry [10] has estimated H to be 1.178 eV, which worked quite well in calculations of spectra and ionization potentials of several methyl-substituted benzenes. With reference to our Fig. 2, Flurry's value of H is well beyond the cross-over point of S_r^P, so that even a large error in his estimate of H will not affect the order of reactive positions as measured by S_r^P.

The reasons for the near-equivalence of the ω- and the PPP-treatments[3] may be sought, first, in the fact that on the present model the methyl substitution represents a relatively small perturbation of the basic naphthalene (alternant) system. Note, for example, that the parameter H, which is a measure of this perturbation, is always quite small (cf. Figs. 1–3) compared with I_c or γ_{rr} (≈ 11 eV). The second reason is that in the parameterization used here, Eqs. (1, 3) and (2, 4) are not only functionally equivalent for a small perturbation, but the leading variable (position-dependent) terms are numerically of the same order of magnitude. Thus for a small perturbation $q_s \approx 1$, and Eq. (3) becomes

$$\alpha_r \approx (\alpha_r)_{\text{core}} + \frac{1}{2} q_r \gamma_{rr} , \tag{3'}$$

which may be compared with the rearranged Eq. (1)

$$\alpha_r = (\alpha + \omega \beta) - q_r \omega \beta , \tag{1'}$$

where the superscripts referring to the number of iterations have been dropped. Eqs. (1') and (3') are functionally equivalent, and the ratio of variable terms is

$$R_{3',1'} = \frac{0.5 \, \gamma_{rr}}{-\omega \beta} .$$

Turning now to Eq. (2), we may observe that since the square bracket in the exponential is less than unity (in particular, $p_{rs} < 1$), the exponential may be approximated by $\exp[\ldots] \approx 1 - [\ldots]$, so that the Eq. (2) becomes

$$\beta_{rs} \approx \beta(1 - 2.683 \times 0.12) + 2.683 \times 0.18 \, p_{rs}\beta , \tag{2'}$$

which is again functionally equivalent to the PPP Eq. (4). The ratio of variable terms is now

$$R_{4,2'} = \frac{-0.5\gamma_{rs}}{0.48\beta} .$$

Using for the Hückel β the usual approximate value $\beta \approx -3$ eV, and with $\gamma_{rr} \approx 11.1$ eV, $\gamma_{rs} \approx 7.8$ eV, we find

$$R_{3',1'} \approx 1.3; \quad R_{4,2'} \approx 2.7 ,$$

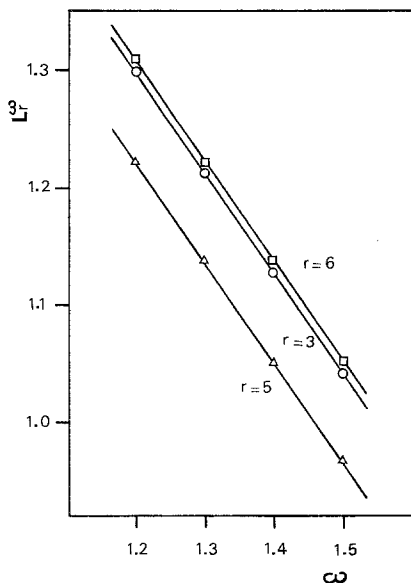[3] We have benefited from the referee's comments on this point.

Fig. 4. Localization energy of 1,4-dimethyl naphthalene L_r^ω at position r, as a function of ω, with $h = -0.2$

so that $R_{3',1'}$ and $R_{4,2'}$ are both of the order of unity, which no doubt accounts for the close numerical agreement between the ω- and the PPP-treatments. It is unlikely, however, that a similar agreement would be found in the case of a larger perturbation or a different parameterization.

Fig. 4 shows the dependence of L_r^ω on ω for one particular value of h. The dependence is strictly linear, so that the order of reactive positions is unaffected. The same is true of the other two reactive indices as a function of ω, except that in these two cases the effect of ω is much less important. These findings confirm an earlier conclusion of Ehrenson [11].

The present results show that S_r, which may be termed a "static" index, is the only reactivity index that correctly predicts not only the most reactive position, but also the order of reactivity of the remaining positions. However we do not wish to insist too much on this agreement, because the failure of the "dynamic" index L_r^ω or L_r^P may just as well be due to the method of calculation. It is probably not quite right to assume, as we have done, that in the "residual molecule" the α or γ_{rr} of the methyl-substituted carbon is changed by the same amount as in the original molecule, regardless of the site of attack by the reagent. In the absence of any definite information, the change in α or γ_{rr} of the "residual molecule" that should be applied can only be conjectured. Because of this uncertainty, the localization energy L_r^ω or L_r^P calculated on the inductive model is subject to some doubt. A sensitivity of L_r to the method of calculation has been noted previously even in simpler systems [12].

Conclusions

With less expenditure of computer time, the ω-technique yields results that are identical to those obtained by the PPP technique. In calculations using a reactivity index like the localization energy which involves an ill-defined transition

state structure, the greater sophistication of the PPP technique may actually be a handicap because of the uncertainty about the numerical values of the various parameters that must be assigned to the transition state. The PPP formalism does permit a more rational determination of the value of the inductive parameter H, but the present results show that it can be directly translated into the ω-technique parameter h.

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