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A quantified resonance theory and its relation with MO – excited state behaviour of conjugated hydrocarbons and heteroconjugate molecules

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Summary. Quantified resonance theory (QRT) involving the use of weight has been applied successfully to ionization potential, electron affinity, energy of the lowest $\pi \rightarrow \pi^*$ transition, charge density and bond order in excited state for alternant and nonalternant hydrocarbons and heteroconjugate molecules. A number of close relations between QRT and HMO or PMO are found. QRT naturally leads to the frontier orbital theory results, and the "natural hypsochromic shift" in electronic spectra of fulvenes is also explained satisfactorily.

Key words: Resonance theory — Resonance energy — Bond order — Charge density — Resonance structures

Introduction

During recent years progress has been made in quantification of the resonance theory (*RT*) of organic chemistry. On the basis of a postulate that all principal resonance structures (*RS*) of a molecule have the same weight, Herndon proposed the structure-resonance theory [1] and showed that an algorithm, logarithm of the resonance structure count (*SC*), gives resonance energies (*RE*) which are in excellent agreement with those obtained from SCF-MO or experiments for various π-hydrocarbon systems, such as neutral hydrocarbons, radicals, anions, cations and radical cations [2]. The most extensive use of Herndon's resonance theory approach (HRT) has been to calculate *RE*, applications of HRT to numerous physical and chemical properties were summarized in a review [3]. On the other hand, our works [4, 5] for quantification of *RT* progresses along another line, that is, the attention is focused simultaneously on *RE*, bond order P_{rs} and charge density q_r, and trying to expose the relationship between *RT* and MO theory, HMO or PMO theory in particular. In line with such an aim, for odd alternant hydrocarbons (*AH*) we proposed recently a scheme [5, 6] for assessing the proper weight to be assigned to the RS_s, that is, the RS_s are divided into sets according as the unpaired electron (or charge) is located at different positions *r*, and the weight W_r of every *RS* in each set is estimated with a formula similar to the Boltzmann distribution equation:

$$W_r = \exp(C\,RE_r) \qquad (C = 1/1.185) \tag{1}$$

in which RE_r is the *RE* of the *r* set, i.e. an even *AH*. By use of this treatment not only *RE* calculated by the algorithm, ln *SC*, are still very good, but also the bond order and charge density obtained by superposing RS_s agree well with MO or experiments. Because the resonance theory treatment of heteroconjugate systems and nonalternant hydrocarbons (*NAH*) may be reduced to the problem of odd *AH* and even *AH*, the quantified resonance theory (QRT) involving the use of weights can be applied successfully to a wide range of conjugate molecules. In addition, a large number of close relations between QRT and HMO or PMO theory were found [4, 5]. Hence the fundamental ideas of classical resonance theory, i.e. stability increases with the number of *RS*; P_{rs} and q_r are obtained by superposing RS_s, in practice, are justified to be correct wholly for these systems, which may be quantified as follows:

$$RE = k \ln SC + k', \tag{2}$$

$$P_{rs} = ND/SC, \tag{3}$$

$$q_r = NC/SC, \tag{4}$$

where *ND* is the count of RS_s in which the *r–s* bond is double, and *NC* is the count of RS_s with a formal charge at position *r*.

So far the correspondence between QRT characterized by Eqs. (2)–(4) and MO theory has been only justified for ground state (R^g) behaviour of molecules. To check further the range of application of QRT in this paper, various experimental quantities related to the frontier orbitals in MO such as ionization potentials *I*, polarographic oxidation potentials $E_{1/2}$(oxi), polarographic reduction potentials $E_{1/2}$(red), and the first $\pi \rightarrow \pi^*$ transition $\lambda_{\max}$, and the theoretical indices q_r and P_{rs} of corresponding ions or electronically excited states (R^e) are calculated by QRT. The results show that extensive agreement between QRT and MO or experiments still exists. Thus the close relationship between *RT* and MO theory is further brought to light.

Even alternant hydrocarbons

With the equal weight assumption, Herndon has already calculated *I* and $E_{1/2}$(oxi) [8, 9]. The procedure of the present QRT treatment is similar to that of HRT. That is, the RS_s of various R^e are just those in conventional qualitative theory of resonance. For instance, for butadiene,

$$\begin{array}{l} \xrightarrow{-e} \overset{+}{C}H_2-\overset{\cdot}{C}H-CH{=}CH_2 \leftrightarrow \overset{+}{C}H_2-CH{=}CH-\overset{\cdot}{C}H_2 \leftrightarrow \cdots \\ CH_2{=}CH-CH{=}CH_2 \xrightarrow{+e} \overset{-}{C}H_2-\overset{\cdot}{C}H-CH{=}CH_2 \leftrightarrow \overset{-}{C}H_2-CH{=}CH-\overset{\cdot}{C}H_2 \leftrightarrow \cdots \\ \xrightarrow{h\nu} \overset{+}{C}H_2-\overset{-}{C}H-CH{=}CH_2 \leftrightarrow \overset{+}{C}H_2-CH{=}CH-\overset{-}{C}H_2 \leftrightarrow \cdots \end{array} \tag{5}$$

(1) A rule for drawing all RS_s of a R^e [10] obviously is: let any one charge or unpaired electron be fixed at an atom in the species and draw the RS_s of the remaining ion or radical. Then the fixing procedure is repeated one by one over all atoms of the R^e, all the RS_s that can be drawn are just the RS_s of this R^e. For even *AH* of *n* atoms after each fixing of an atom one gets an odd *AH*, so that the total number of RS_s for a R^e reduces to calculating unnormalized NBMO coefficients b_{0i} of *n* odd *AH* according to the zero-sum rule [11].

(2) A corollary follows immediately from (1): for a R^e the RS_s of all RS_s that a certain charge appears at atom *r* are just those RS_s that can be written with this charge fixed at *r*, and the number of this RS_s may thus be obtained from b_{0i} of one odd *AH*. Therefore the calculation of q_r by Eq. (4) is a simple one.

(3) The weight-corrected total structure count (SC_w^e) of a R^e is calculated by the procedure which is the same as that for odd *AH*, that is, the RS_s are divided into sets according as one charge or unpaired electron is located at different positions. The weight of every *RS* in each set is still estimated with the QRT formula (1), in which RE_r is the *RE*, in this case, of an odd *AH*. It is known for odd *AH* [4] that $k = 0.593$ and $k' = 0$ in Eq. (2),

$$RE_r = 0.593 \ln SC_w, \tag{6}$$

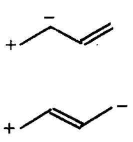
where $SC_w = \sum b_{0i}^2$ and $SC_w^+ = SC_w^- = SC_w^{\cdot} \equiv SC_w$ that is the weight-corrected total *SC* of the odd *AH* [4]. By substituting Eq. (6) into Eq. (1) we have

$$W_r = SC_w^{0.5}.$$

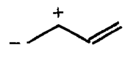
Thus the SC_w^e (i.e. SC_w^{+-}, $SC_w^{+\cdot}$ and $SC_w^{-\cdot}$) of a R^e is

$$SC_w^e = \sum_r (SC_w \times SC_w^{0.5})_r = \sum_r (SC_w^{1.5})_r, \tag{7}$$

where the sum is over all the positions in a molecule, for example butadiene has 6 RS_s, using the procedure of fixing (+) they may be listed as follows:



Set 1



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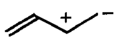

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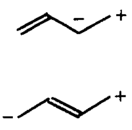
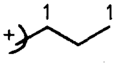


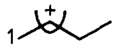
Set 4

The odd AH formed with (+) fixed at atom 1 (i.e. set 1) and its b_{0i} are



$$(SC_w)_1 = \left(\sum b_{0i}^2\right)_1 = 1^2 + 1^2 = 2.$$

For set 2

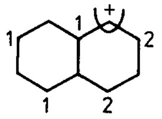


$$(SC_w)_2 = \left(\sum b_{0i}^2\right)_2 = 1^2 = 1.$$

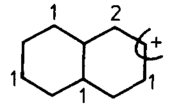
According to Eq. (7) for butadiene

$$SC_w^e = 2(2^{1.5} + 1) = 7.66.$$

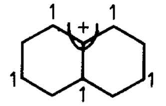
Similarly for naphthalene



$(b_{0i})_1$



$(b_{0i})_2$



$(b_{0i})_9$

$(SC_w)_r$ are:

$2^2 + 2^2 + 1^2 + 1^2 + 1^2 = 11$ $\quad 2^2 + 1^2 + 1^2 + 1^2 + 1^2 = 8$ $\quad 1^2 + 1^2 + 1^2 + 1^2 + 1^2 = 5$

thus

$$SC_w^e = 4(11^{1.5} + 8^{1.5}) + 2 \times 5^{1.5} = 258.8.$$

On the other hand, if the equal weight assumption is taken, as Herndon did, the total structure count SC^e of the R^e will simply be $\sum_r (\sum b_{0i})_r$, evidently SC_w^e must be greater than SC^e regularly, in fact, SC_w^e and SC^e are in a close linear correlation, for example, for 29 even AH listed in [9] $SC_w^e : SC^e$ $r = 0.997$, thus both will give similar results on the correlations with experimental data.

(4) The properties related to frontier orbitals such as I, A (electron affinity) and ΔE (energy of the lowest $\pi \rightarrow \pi^*$ transition) may also be calculated theoretically by difference from the total energies of a parent hydrocarbon and the corresponding R^e [9, 12]. Assuming either that there is no gross molecular structural change in the underlying σ framework upon ionization [9] or that the energies of this changes are approximately a constant for the same $R^g \rightarrow R^e$ process of a series of similar molecules, then the I, A, ΔE and related experimental quantities (Exp^e), as Herndon indicated [8, 9], should be linearly related to the difference in π-stabilization energies of the neutral compound and the corresponding R^e, i.e.

$$\mathrm{Exp}^e = a(RE^g - RE^e) + a'. \tag{8}$$

It is known that $RE^g = 1.185 \ln SC^g$ [3], and using Eq. (2) for R^e one can rewrite Eq. (8) as

$$\mathrm{Exp}^e = c(\ln SC^g - k \ln SC_w^e) + c'. \tag{9}$$

(5) To test the applicability of Eq. (9) as much of Exp^e were used as possible in the present work. For $E_{1/2}(\mathrm{oxi})$ and $E_{1/2}(\mathrm{red})$, as other theoretical methods did, the correlated compounds include also fluoranthenoid hydrocarbons etc. [8, 12] (for QRT treatment of *NAH* see the following section); I denotes the photoelectron spectra values [13–15]; and ΔE or $\lambda_{\max}$ are values of the p-band of aromatic compounds [13–15]. Multiple regression analysis of the data using Eq. (9) gives

$$E_{1/2}(\mathrm{oxi})\ (\mathrm{V}) = 1.940(\ln SC^g - 0.32 \ln SC_w^{+\cdot}) + 2.967,$$

$$I\ (\mathrm{eV}) = 1.781(\ln SC^g - 0.36 \ln SC_w^{+\cdot}) + 9.790,$$

$$E_{1/2}(\mathrm{red})\ (\mathrm{V}) = 1.815(\ln SC^g - 0.32 \ln SC_w^{-\cdot}) + 3.268,$$

$$\lambda_{\max}\ (\mathrm{nm}) = -386(\ln SC^g - 0.32 \ln SC_w^{+-}) - 12,$$

the correlation coefficients (r) for the relationship between the experimental quantities and various theoretical values, average deviations and (n) the number of compounds included in the correlations are summarized in Table 1.

It can be seen from Table 1 that the different theoretical methods compared in the present work are about equally effective in correlating various expeirmental quantities.

(6) The charge density q_r in a R^e is obtained from Eq. (4)

$$q_r = (SC_w^{1.5})_r / SC_w^e. \tag{10}$$

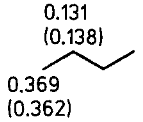
in which, as mentioned in (3), the $(SC_w)_r$ is a weight-corrected *SC* of an odd *AH* formed with this charge fixed at atom r in R^e. Since an odd *AH* has an identical SC_w value whether it is a cation, anion or radical and from (3) the total *SC* of various R_s^e for even AH_s also have an identical value for SC_w^e, QRT gives a conclusion that $q_r^+ = q_r^- = q_r^{\cdot} \equiv q_r^f$ (QRT) for all the R^e of an even *AH*. It is noteworthy that the conclusion is in accord with HMO theory (the pairing theorem of MO), and q_r^f(QRT) corresponds to the frontier electron density in HMO. The q_r^f(QRT) parallel q_r^f(HMO), both almost always give the same position at which the q_r^f is the maximum in a molecule. The QRT(HMO) q_r^f

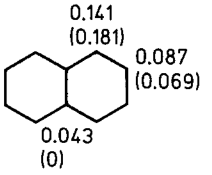
Table 1. Experimental quantities-theoretical values correlations, $r(n)$ ave.dev.

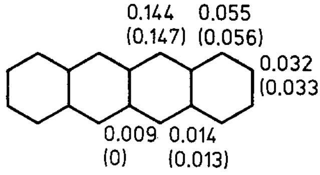
	HRT [8, 9]	QRT	HMO [8, 12]	SCF-MO [12, 16]
$E_{1/2}(\mathrm{oxi})$	0.931(25)0.092	0.959(25)0.075	0.922(25)0.088	0.926(25)0.07
$E_{1/2}(\mathrm{red})$		0.961(76)0.080	0.970(76)0.068	0.967(76)0.07
I	0.974(29)0.160	0.974(63)0.087	0.961(63)0.108	
$\lambda_{\max}$ or $\nu_{\max}$		0.966(60)[a]	0.979(60)[b]	

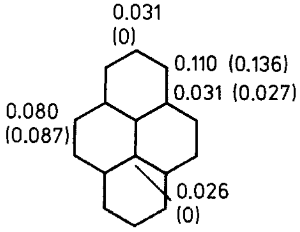
[a] $\lambda_{\max}$; [b] $\nu_{\max}$

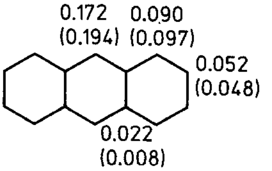
values of a few molecules of general interest are listed as follows:

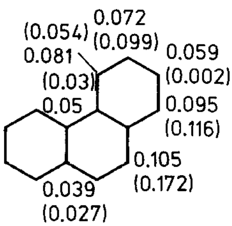








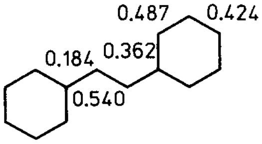


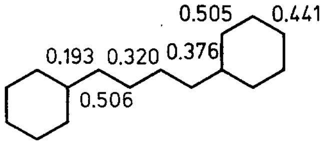


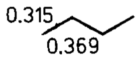
(7) Because the $(SC_w)_r$ in Eq. (10) is just the structure count of the substitution reaction intermediate at position r for the parent hydrocarbon [4] and the SC_w^e is a constant only for a certain parent molecule, QRT yields a conclusion that the larger the q_r^f(QRT) is, the more reactive the r position would be. But this only applies to prediction concerning the order of reactivity of each position in a given molecule. Thus QRT leads naturally to the results given by the frontier orbital theory [17].

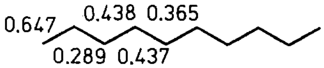
(8) According to (6) since $q_r^+ = q_r^-$, the formal charge at every atom in a R^{+-} is zero, therefore the R^{+-} of even AH will have no π-dipole moment, which again is in accordance with HMO theory.

(9) The bond order P_{rs}^e calculated from Eq. (3) for R^e and the change in P_{rs} from R^g to R^e are similar to those given by HMO or SCF-MO, that is: 1. The sum of P_{rs}^e is less than that of P_{rs}^g for a given molecule, from QRT $\sum P_{rs}^g - \sum P_{rs}^e = 1$ (see formulae 5), and from HMO whether an electron is added to antibonding LUMO or is lost from the bonding HOMO causes a decrease in total binding energy and thus must correspond to a decrease in $\sum P_{rs}$. 2. Upon $R^g \rightarrow R^e$, for linear polyenes or α,ω-diphenylpolyenes the bond alternation in the polyene chain is weakened, i.e. single → double bond and double → single bond, and the effect is most prominent in the middle portion of the molecules [18, 19]. 3. From the argument precisely similar to that used in (6) QRT gives $P_{rs}^{+\cdot} = P_{rs}^{-\cdot} = P_{rs}^{+-} \equiv P_{rs}^e$ for a given even AH, whereas according to HMO $P_{rs}^{+\cdot} = P_{rs}^{-\cdot} \neq P_{rs}^{+-}$. The situation in bond alternation obtained by QRT P_{rs}^e is about that between $P_{rs}^{+\cdot}$ and P_{rs}^{+-} given by HMO. In the following the QRT P_{rs}^e for a few molecules are listed, note that the P_{rs}^g(QRT) in the polyene chain are simply 1 or 0, and 0.5 in benzene ring.









Even alternant heteroconjugate molecules

(10) *I and A*. Take quinoline as an example, for which the calculation of $SC_w^{+\cdot}$ and $SC_w^{-\cdot}$ differs from naphthalene only in that the weight of those RS_s that the $(-)$ or $(+)$ is assigned to the more electronegative N atom should be greater or less than unity, respectively, i.e. $(1+m)$ or $(1-m)$, where m characterizes the perturbation of weight due to a change in electronegativity of atom [5]. Take the calculation of $SC_w^{+\cdot}$ as an example: let $(SC_w)_t \equiv B_t$ be the SC_w of an odd AH formed with the $(+)$ fixed at position t of the hetero-atom in the parent hydrocarbon, and then from the rule for drawing all the RS_s of a R^e mentioned in (1) and by comparing $SC_w^{+\cdot}$ of the hetero-system with that of the isoconjugate hydrocarbon we have

$$\begin{aligned} SC_w^{+\cdot}(\text{hetero}) &= SC_w^{+\cdot}(\text{hydroc}) - B_t^{1.5} + B_t^{1.5}(1-m) \\ &= SC_w^{+\cdot}(\text{hydroc}) - B_t^{1.5}m. \end{aligned} \tag{11}$$

It is known that the k and k' values in Eq. (2) for RE^g of heteroconjugate molecules are the same as or quite close to that for isoconjugate AH [4], we may reasonably assume that the same is true for RE^e. Thus

$$\begin{aligned} RE^{+\cdot}(\text{hetero}) - RE^{+\cdot}(\text{hydroc}) = k[\ln(&SC_w^{+\cdot}(\text{hydroc}) \\ &- B_t^{1.5}m) - \ln SC_w^{+\cdot}(\text{hydroc})] \end{aligned}$$

noticing Eq. (10) we obtain $\quad = k\ln(1 - q_t^f m)$.

Evidently the situation will be similar for $SC_w^{-\cdot}$

$$SC_w^{-\cdot}(\text{hetero}) = SC_w^{-\cdot}(\text{hydroc}) + B_t^{1.5}m \tag{12}$$

and

$$RE^{-\cdot}(\text{hetero}) - RE^{-\cdot}(\text{hydroc}) = k\ln(1 + q_t^f m).$$

Using the same approximation as that in PMO theory [5], i.e.

$$RE^g(\text{hetero}) = RE^g(\text{hydroc}) \tag{13}$$

and from Eq. (8) QRT obtains the results which are in accord with PMO theory

[20], that is, replacing a carbon atom in an even AH by a more electronegative heteroatom leads to an increase in I and A, and the increments depend on the "frontier electron density" at the position in question.

QRT	PMO
$\Delta I = I(\text{hetero}) - I(\text{hydroc}) = -K' \ln(1 - q_t^f m)$	$\Delta E(\text{HOMO}) = q_t^f \, \Delta\alpha$
$\Delta A = A(\text{hetero}) - A(\text{hydroc}) = K' \ln(1 + q_t^f m)$	$\Delta E(\text{LUMO}) = q_t^f \, \Delta\alpha.$

(11) *The energy of the lowest* $\pi \rightarrow \pi^*$ *transition* ΔE. Before considering the calculation of $SC_w^{+-}(\text{hetero})$ let us point out a relation among the structure counts of various R^e for a given molecule

$$SC_w^{+-} - SC_w^{+\cdot} = SC_w^{-\cdot} - SC_w^{\cdot\cdot} \tag{14}$$

the hold of Eq. (14) can be seen from the following discussion. By use of the procedure wherein a charge is fixed and all RS_s are drawn up, as mentioned in (1), all the same RS_s of this R^e will be drawn independently of the interchange of location of the two unpaired sites. It is easy to see that when a fixed (+) is choosen for both SC_w^{+-} and $SC_w^{+\cdot}$ the left-hand side of Eq. (14) represents a sum of difference of $SC_w^{1.5}$ between radical anion and radical of the identical hetero-odd-AH_s $\Delta = \sum_i [(SC_w^-)^{1.5} - (SC_w^{\cdot})^{1.5}]_i$. Similarly we get that the right-hand side of Eq. (14) represents just an identical Δ value when the fixing (·) procedure is used. Since $SC_w^{\cdot\cdot}$ for heteroconjugate molecules is equal to SC_w^e for corresponding isoconjugate hydrocarbons [5], Eq. (14) may be written as

$$SC_w^{+-}(\text{hetero}) = SC_w^{-\cdot}(\text{hetero}) + SC_w^{+\cdot}(\text{hetero}) - SC_w^e(\text{hydroc}). \tag{15}$$

Substituting Eqs. (11) and (12) into Eq. (15) and noticing (3),

$$SC_w^{+-}(\text{hetero}) = SC_w^{+-}(\text{hydroc}).$$

using Eq. (13) we get

$$\Delta E(\text{hetero}) = \Delta E(\text{hydroc}).$$

This is again in accordance with PMO theory [20].

(12) According to HMO, q_r^{ho} and q_r^{lu} (the density of electron in HOMO and LUMO) are just the density of the unpaired electron (·) in $R^{+\cdot}$ and $R^{-\cdot}$, respectively. On the other hand from QRT, as mentioned in (3), these densities can be expressed as

$$q_r^{\text{ho}}(\text{QRT}) = (SC_w^+)_r^{1.5}/SC_w^{+\cdot}; \qquad q_r^{\text{lu}}(\text{QRT}) = (SC_w^-)_r^{1.5}/SC_w^{-\cdot}. \tag{16}$$

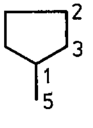
where $(SC_w^+)_r$ and $(SC_w^-)_r$ are the structure counts of the hetero odd AH which is formed with this (·) fixed at atom r in the $R^{+\cdot}$ and $R^{-\cdot}$ respectively. It is easily seen that $(SC_w^+)_r$ and $(SC_w^-)_r$ in Eqs. (16) are just the structure counts of the reaction intermediates of electrophilic and nucleophilic substitutions respectively for the parent molecule, and $SC_w^{+\cdot}$ or $SC_w^{-\cdot}$ is a constant for a given molecule. Thus QRT yields a conclusion that q_r^{ho} and q_r^{lu} at various positions in a molecule should serve as a measure of reactivity for electrophilic and nucleophilic substitution, respectively, but it does not permit comparison between different molecules.

This corresponds to the result that frontier orbital theory can be extended to hetero even AH [21].

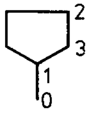
(13) It was proved [5] that for hetero even AH the QRT localization energies of electrophilic and nucleophilic substitutions, that are calculated from $(SC_w^+)_r$ and $(SC_w^-)_r$ in Eq. (16), are in excellent agreement with the corresponding PMO localized energies or experiments. On the other hand, as has been shown from the frontier orbital theory $q_r^{\mathrm{ho}}(\mathrm{HMO})$ and $q_r^{\mathrm{lu}}(\mathrm{HMO})$ are parallel to the experimental data, thus there must be a parallelism of $q_r^f(\mathrm{QRT})$ and $q_r^f(\mathrm{HMO})$ for a given hetero-molecule.

Even NAH containing a 5- or 7-membered ring

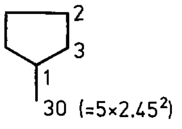
(14) SC_w^e *of even* NAH. Because in a NAH the 5- or 7-membered ring having a tendency to satisfy the $(4n+2)$ rule is an electron-attracting or electron-repelling group respectively, a molecule containing an odd-membered ring may be regarded as a "hetero-system" [5]. To calculate $SC_w^{+\cdot}$ and $SC_w^{-\cdot}$, as has been said before, one may choose conveniently the procedure of fixing $(\cdot)$, so that this problem is actually reduced to calculations of $(SC_w^+)_r$ and $(SC_w^-)_r$ i.e. structure counts of reaction intermediates for electrophilic and nucleophilic substitutions, respectively. Then from Eq. (7) $SC_w^{+\cdot}=\sum_r (SC_w^+)_r^{1.5}$ and $SC_w^{-\cdot}=\sum_r (SC_w^-)_r^{1.5}$, the detailed calculation method for these intermediates has been given in a previous paper [5]. The basic principle is: the RS_s for which the odd-membered ring forms a $(4n)$ conjugated circuit are excluded [5, 7], whereas those RS_s that the odd-membered ring forms an 6-electron conjugated circuit have greater weight $(1+m)$, and for $(5)^-$ $(1+m)=2.45$; for $(7)^+$ $(1+m)=1.77$. On the other hand, the reaction intermediate for radical substitution of this parent NAH has no RS for which the odd-membered ring forms $(4n)$ or $(4n+2)$ conjugated circuit, so that every $(SC_w^{\cdot})_r$ can simply be obtained by calculating NBMO coefficients twice [5], for example the fulvene molecule,



$(SC_w^{\cdot})_r$



$(SC_w^+)_r$



$(SC_w^-)_r$

Thus we get a result for even NAH,

$$SC_w^{+\cdot} \neq SC_w^{-\cdot} \neq SC_w^{\cdot\cdot}$$

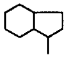
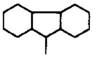
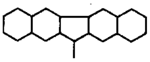
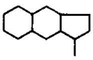
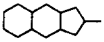
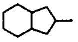
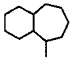
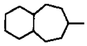
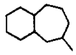
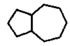
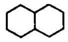
which is different from that for even AH. Finally the SC_w^{+-} is calculated from Eq. (14).

(15) It is known [5] that for this kind of NAH

$$RE^g = 1.185 \ln SC^g - 0.25,$$

using Eq. (2) for R^e in the same way as in (4) we obtain the conclusion that Eq.

Table 2. Structure counts and lowest $\pi \rightarrow \pi^*$ transition energies

	$SC_w^{+\cdot}$	$SC_w^{-\cdot}$	$SC_w^{\cdot\cdot}$	SC_w^{+-}	SC^g	$\ln SC^g - 0.32 \ln SC_w^{+-}$	HMO $\Delta E(-\beta)$
	17.05	181	28.2	170	1	-1.643	0.872
	125.5	421	168.9	378	2	-1.206	0.925
	1005	1627	1144	1488	4	-0.951	1.069
	21999	24134	22653	23480	9	-1.023	0.969
	663	1165	767	1061	3	-1.131	0.809
	540	1048	644	944	1	-2.192	0.254
	121	416	164	373	1	-1.895	0.428
	136	33.1	51.6	118	1	-1.527	0.661
	454	223	294	383	2	-1.210	0.719
	417	186	257	346	2	-1.178	0.845
	430	199	270	359	1	-1.883	0.347
	285	601	157	729	2	-1.416	0.877
	259	259	259	259	3	-0.680	1.236
	31.2	31.2	31.2	31.2	2	-0.408	2.000

(9) still holds for even *NAH*. Using Eq. (9) and the same k value of 0.32, it was found that $E_{1/2}(\text{oxi})$ and $E_{1/2}(\text{red})$ of a fluoranthenoid series and a few other *NAH* fall on the same regression lines as the values for *AH*, which is in accordance with MO theory. The results of statistical treatment have been given in (5) and Table 1.

In Table 2 the QRT($\ln SC^g - 0.32 \ln SC_w^{+-}$) are compared with HMO lowest $\pi \rightarrow \pi^*$ transition energy ΔE for some *NAH* of general interest. The results show that both are parallel to each other, and the "natural hypsochromic sift" [22] in electronic spectra of some *NAH* is also explained satisfactorily by QRT.

(16) From (12) we still get that the larger the $q_r^{\text{ho}}(\text{QRT})$ or $q_r^{\text{lu}}(\text{QRT})$ is, the more active the r position would be for electrophilic or nucleophilic substitution, respectively.

Conclusions

QRT is essentially a quantification of the widely used but purely qualitative theory of resonance in organic chemistry. Although the *RT* has enjoyed a great popularity for many years, there have been different opinions [23, 24] about the nature and correctness of this theory. The present paper and our previous works [4, 5] have demonstrated that the fundamental ideas of *RT* are correct wholy; taking weights of RS_s into account the three basic indices *RE*, P_{rs} and q_r can be calculated simultaneously from RS_s of a conjugated molecule, and the results are in extensive agreement with experiments or MO for not only the ground state but also the excited states. In addition, a large number of close relations between QRT and HMO or PMO results are indicated. Thus the correspondence between *RT* and MO theory and a wide developing future that the QRT could have are illustrated.

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