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(52) The enthalpies in Figure 1 are not corrected for the tendency of MM2 to underestimate the steric energy of congested rotational barriers, in order to keep continuity of the potential curve.

(53) The rotation of *tert*-butyl groups from **1B** to 1F′ and 1F″ is the result of forced, concerted, two-bond drive, and hence must be distinguished from "correlated rotation" of *tert*-butyl groups in tri-*tert*-butylsilane (W. D. Hounshell, L. D. Iroff, R. J. Wroczynski, and K. Mislow, *J. Am. Chem. Soc.*, **100**, 5212 (1978)), wherein the passage from one energy minimum to another leads to a permutational exchange in the ligands of both rotors when one is driven and the other follows.

(54) That both 1F′ and 1F″ are true energy minima was confirmed by freely relaxing several conformations near **1F**′ and 1F″ obtained in the course of the second drive calculations. Relaxation of 1F without any constraint led to 1F′.

(55) The lowest energy path from **1B** to 1F′ (or **1F**″) will probably involve concerted three-bond rotation wherein two C_t–C_q bonds and the central C_t–C_t bond rotate more or less simultaneously. It is approximately correct to think that the transformation involves crossing over at the apparent cross point G (or G′) between the solid and dotted lines (Figure 3). At this point and between the solid and dotted lines lie a barrier similar to that depicted between **1B** and **1F** with dashed line.

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Direct Calculation of Resonance Energies of Conjugated Hydrocarbons with ab Initio MO Methods

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Abstract: Resonance energies of conjugated hydrocarbons were calculated as the energy difference between the ab initio SCF energy and the energy expectation value with respect to a model wave function in which the SCF π orbitals were replaced by appropriate nonresonating localized π MOs (reference state). The contributions of electron correlation and of relaxation of σ orbitals on resonance energies were also computed and found to be rather small in most cases. Since all electrons were included in the calculations, vertical and adiabatic resonance energies could be obtained. The adiabatic resonance energy of butadiene, which was computed to be about 9 kcal/mol, has partly to compensate for the unfavorable repulsion of the two nonresonating π MOs in the reference state. The resonance energies of other hydrocarbons were normalized with respect to butadiene and could thus be compared with thermochemical resonance energies. The largest molecules studied were naphthalene and azulene. The SCF calculations on the latter system gave evidence that azulene probably has a structure with bonds of alternate lengths.

I. Introduction

Originally, the resonance energy of a conjugated hydrocarbon was conceived as the enthalpy difference between the conjugated system and its reference state containing localized nonresonating double bonds.[1-5] The heat of formation of the latter model compound is not a measurable quantity but was deduced from additivity relationships with bond increments taken from compounds without conjugated double bonds.[2-5] However, there is no unique method for the determination of

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the energy which has to be ascribed to the sp^2-sp^2 C-C single bond without conjugation.[6] Consequently, different sets of resonance energies have been proposed[2,5,6] with the resonance energy of benzene varying from 20[6] to 41 kcal/mol.[5] Thus, the concept of resonance energies was subjected to serious criticism.[8] A solution to this problem was offered by Dewar et al.,[6,7] who derived the bond energies to be used in additivity rules for reference states from a linear regression of (theoretically calculated) heats of atomization of linear polyenes and of radialenes. The resonance energies of polyenes were thus defined to be zero. The Dewar resonance energy of a conjugated hydrocarbon is a direct measure of its stability in comparison with an analogous classical polyene rather than with a hypothetical model compound with nonresonating double bonds. Since Dewar's bond energies differ from those derived from hydrocarbons without conjugated double bonds mainly in the energy ascribed to the C-C single bond, resonance energies of different sets can be normalized with respect to butadiene according to the equation

$$\mathrm{RE_N} = \mathrm{RE} - n\mathrm{RE(butadiene)} \qquad (1)$$

where n is the number of single bonds in the reference state. Normalized resonance energies from different sets agree reasonably well among each other. They are essentially equivalent to Dewar's resonance energies.

Recently, the heat of homodesmotic reactions was used for the definition of resonance energies.[9] For benzene a resonance energy of 21.2 kcal/mol was obtained as the heat of the reaction

$$\text{benzene} + 3\ \text{ethylene} \rightarrow 3\ \text{butadiene}$$

Evidently, such a definition is equivalent to the normalization of the resonance energy of benzene with respect to that of butadiene. The same authors proposed butadiene with the C-C single bond rotated by 90° to be taken as the reference molecule for the definition of resonance energies.[9b] The (planar) butadiene itself would then have a resonance energy of 7.2 kcal/mol (=barrier of rotation around the single bond[10]). The latter procedure would correspond to nothing more than a renormalization of resonance energies.

The basic understanding of resonance in conjugated π systems was one of the outstanding successes of the Hückel π theory[1,3] especially in its PMO formulation.[6] However, Hückel resonance energies which are obtained in energy units β do not show a good proportionality with any set of empirical resonance energies. With PPP π theory[11] and empirical σ bond potential functions, Dewar et al.,[6,7] Whitehead and Lo,[12] and recently Kao and Allinger[13] were able to compute heats of atomization of conjugated hydrocarbons with high accuracy. From computed heats of atomization resonance energies could be deduced which were defined exactly in the same way as Dewar's empirical resonance energies. In recent years, elaborate schemes using in some cases valence bond and graph theoretical formalism have been reported[14,15] which allow the normalization of Hückel resonance energies yielding resonance energies which agree well with those of Dewar et al.[7] On the level of all-valence-electron and of ab initio SCF theories, the calculated heats of homodesmotic and of isodesmic[17] reactions were used for the definition of resonance energies.[9,16,18]

The Dewar resonance energy of a conjugated system, whether calculated theoretically or derived from thermochemical data, does not represent the amount of energy which is gained in the system by resonance of the double-bond orbitals. The purpose of the present work has been finding answers to the following questions: How much energy is really gained by the delocalization of the electrons in a conjugated system? How can this energy gain be defined and computed within an ab initio MO theory? Is there any relationship between theoretically computed resonance energies and corresponding thermochemical quantities? Can our theoretical approach also be applied for the quantification of other models used in chemistry?

II. Methods for the Direct Calculation of Resonance Energies

We are interested in the calculation of the resonance energy of a conjugated hydrocarbon in its original sense as the energy difference between the conjugated system and its reference state without resonance. How the energy of such a reference state can be calculated is most easily understood on the level of Hückel π theory where we have three different though equivalent methods for the calculation of the π energy $E_\pi{}^\mathrm{R}$ of the reference state: (a) $E_\pi{}^\mathrm{R} = mE(\text{ethylene})$, where m is the number of double bonds in the reference state. (b) $E_\pi{}^\mathrm{R} = \langle E\rangle_\mathrm{LMO}$. The reference state is represented by a model wave function consisting of strictly localized nonresonating π MOs. The π energy of the reference state is obtained as the energy expectation value of the model wave function with respect to the Hückel matrix of the original π system. (c) $E_\pi{}^\mathrm{R} = E_\pi$(nonresonating model). The π energy of the reference state is obtained from a Hückel calculation using a model Hückel operator with all those matrix elements set to zero which correspond to interactions between atomic orbitals separated by a single bond.

These three methods can also be applied within an ab initio SCF theory where they are no longer equivalent:

(a) Though total π energies can be defined within an ab initio SCF formalism, the application of method (a) would not lead to quantities which could be considered as resonance energies. The reason is that the ab initio π energy contains some potential energy contributions from the underlying σ system which have nothing to do with the model of resonance.

(b) This method is based on the computation of an energy expectation value with respect to a model wave function representing a reference state with nonresonant double bond orbitals. Energy expectation values are never lower than the actual energy of the system under consideration and they correspond in principle to measurable physical quantities. The model wave function represents a nonstationary state which cannot be realized in practice, but which has still been used as a reference state for the definition and for the computation of resonance energies. In 1951 Mulliken and Parr calculated the vertical resonance energies of butadiene and of benzene using this method within a nonempirical π theory.[5]

(c) In this method an effective model one-electron Hamiltonian is constructed and the optimum wave function for that model operator is computed. Energies obtained by this procedure can in principle be lower or higher than the energy of the actual system. In addition, the calculated energy is not a real physical quantity since it does not correspond to any state of any real physical system. Though it is quite common to look for solutions of model operators (all semiempirical MO schemes are based on model operators), the interpretation of energy quantities gained from method 4 would certainly be a complex task.

For the computation of resonance energies within this ab initio study, only procedures based on the calculation of energy expectation values (method (b)) have been considered further.

III. Model Wave Functions of the Reference States

The nonresonating π orbitals of a reference state can be constructed by one of the following methods:

(1) Localized π MOs ascribed to the double bonds of the reference state are transferred from a SCF calculation of ethylene. This method is very simple when a minimal basis is

used, while its application becomes fairly complicated when d functions are included in the basis and the double bonds of the conjugated system have different orientations in the coordinate system.

(2) The basis function coefficients of the strictly localized π MOs of the reference state are obtained as the square roots of the corresponding diagonal elements of the bond order matrix of the conjugated system.

(3) The delocalized π MOs can be localized using, for example, the localization according to Boys.[19] The localized orbitals can then be truncated in order to have them strictly localized and nonresonating.

A priori, one cannot give preference to any of the three methods. Actual calculations will show which of the methods yields the lowest energy expectation value for the reference state.

The σ orbitals in the model wave function are in general assumed to remain unchanged when the conjugation of the π orbitals is removed. However, the effect of the reoptimization of the σ orbitals in the model wave function with the nonresonating π orbitals being frozen has been also investigated for butadiene, for benzene, and for some nonalternant hydrocarbon systems.

The wave function of the ground state of a molecule can be represented by more than one determinant in order to allow for electron correlation. The model wave function can also be represented by more than just one determinant. The restrictions to be observed while doing so will be discussed in the next section. The influence of correlation on computed resonance energies has been investigated for butadiene and for benzene.

IV. Computational Methods

The SCF program used is based on the integral program for pure Gaussian lobes developed by Ahlrichs.[20] The following types of basis sets were applied: (1) minimal basis (MB) constructed from 5s and 2p Gaussian lobes for the carbon atom and two Gaussian s lobes for hydrogen (The exponents and the contraction coefficients of the lobes were optimized from molecular calculations.[21]); (2) double ζ basis (DZ), a 7.3/3 basis proposed by Huzinaga[22] coupled to [4,1,1,1.2,1/3] (The three Gaussian lobes at the hydrogen atoms were grouped to one basis orbital with the optimum contraction coefficients taken from a SCF calculation on the hydrogen molecule.); (3) double ζ plus polarization function (DZ + D), which denotes the same basis as DZ except that the basis was augmented by one set of d functions at the carbon atoms with an exponent of 1.0.

A program was written for the construction of model wave functions. The strictly localized π MOs of the model wave function could be symmetry adapted, and were subjected to either a symmetrical or a Schmidt orthogonalization.

The SCF program had options which allowed the computation of energy expectation values with respect to a set of orbitals supplied on an input device. In addition, an arbitrary number of MOs could be kept frozen during the SCF iteration cycles.

In order to study the influence of electron correlation on the computed resonance energies, the correlation energy of the ground state as well as of the reference state was computed by the PMO-CI approach.[23,24] This method is equivalent to a configuration interaction (CI) treatment, in which all double substitutions from a given reference determinant are included. Since single excitations were not included in our treatment, no part of the resonance energy was led in through the back door, when the electron correlation energy for the reference state was computed.

V. Resonance Energy of 1,3-Butadiene

1. The Optimum Model Wave Function for the Reference Structure without Resonance. In section III, three different, nonequivalent methods were given for the construction of nonresonating π MOs for conjugated hydrocarbons. For 1,3-butadiene (**1**) with a C-C single bond length of 1.48 Å all three methods were applied and the following values for the vertical resonance energy were obtained (DZ basis): (1) transfer of ethylene π MOs (9.49 kcal/mol); (2) π MOs constructed from bond order matrix (9.59 kcal/mol); (3) localization and truncation of π MOs (9.51 kcal/mol). All three methods yield almost the same value for the resonance energy. As is confirmed by a calculation with the DZ + D basis on butadiene and by calculations on other π systems, method (2) is slightly inferior to the other methods. Starting from the ethylene π MOs of method (1), we tried to optimize the model wave function further. Within the restriction that the π MOs are not allowed to conjugate with each other, the remaining three degrees of freedom for the π MOs within a DZ basis were optimized: (a) The p_π AOs in the reference state of butadiene want to be slightly more diffuse than they are in ethylene. Energy gain: 0.02 kcal/mol. (b) The π bond orbitals are slightly polarized with the negative charge at the outer C atoms because of their repulsion. Energy gain: 0.003 kcal/mol. (c) The p_π AOs want to be more diffuse at the outer than at the inner carbon atoms. Energy gain: 0.002 kcal/mol.

Thus, the total energy gain from the optimization of orbitals in the reference state is negligible and π MOs constructed by methods (1) or (3) need no further improvement. Hence, the π MOs of the reference state are not subjected to any further variations in the following (the only exception is methylenecyclopropene; cf. section IX).

The σ MOs in the model wave function were those taken from the SCF wave function of butadiene. These σ SCF MOs may no longer be the optimum σ MOs for the reference state of butadiene without resonance. The optimization of the σ MOs with respect to the frozen nonresonating π MOs lowers the energy of the reference state by very small amounts which are increasing with increasing flexibility of the basis, from 0.01 kcal/mol for MB to 0.05 kcal/mol for DZ + D (cf. Table I). We conclude that at least in this case the contribution of σ relaxation to the resonance energy of a conjugated hydrocarbon is negligible.

2. Basis Dependence of the Resonance Energy. In order to ensure that calculated resonance energies are not simply an artifact of a given basis, the resonance energy of butadiene was calculated with three different basis sets. As the results given in Table I show, the vertical resonance energy for a C-C single bond distance of 1.48 Å depends little on the basis set. Even the minimal basis, though yielding a SCF energy of about 1.5 au above the DZ SCF energy, gives a value for the resonance energy which differs only by about 2% from the value obtained with the DZ basis. The vertical resonance energy of butadiene is increased by about 5% when the DZ + D basis is applied instead of DZ. Obviously, the d basis orbitals are mainly strengthening the individual π bonds rather than enhancing conjugation.

Owing to the fact that resonance is primarily a one-electron operator effect, resonance energies can be well reproduced even with a minimal basis and it is not very important to apply more flexible or even basis sets which include polarization functions. This is a very important result with respect to the calculations of resonance energies of large conjugated hydrocarbons, where at most MB SCF calculations can be performed.

3. Vertical and Adiabatic Resonance Energies. A value for the vertical resonance energy is obtained as the difference between the total SCF energy and the energy expectation value with respect to the model wave function for a given reference structure. When resonance energies are computed from π

Table I. Resonance Energy of Butadiene Calculated with Different Basis Sets (in kcal/mol and Bond Lengths in Å)

	MB	DZ	DZ + D
total SCF energy, au[a]	153.2773	154.7087	154.7660
vertical resonance energy[a,b]	9.7	9.5	10.0
contribution of σ relaxation	−0.01	−0.03	−0.05
contribution of correlation[c]	−1.2	−1.1	−0.7
adiabatic resonance energy[b]	8.7	9.3	9.7
contribution of correlation[c]	−1.1	−1.0	−0.6
optimum C-C bond length without resonance[d]	1.526	1.510	1.510
optimum C-C bond length SCF	1.493	1.462	1.463
optimum C-C bond length for C_2H_4 90°[e]	1.486	1.466	1.461
barrier of single bond rotation for butadiene[f]	6.2	6.4	6.6

[a] Bond lengths: C=C 1.34 Å, C—C 1.48 Å, C—H 1.10 Å. [b] Model wave function with ethylene π MOs; without σ relaxation; electron correlation not included. [c] Correlation energy computed with PNO-CI. [d] Optimum bond length for the energy expectation value with respect to the model wave function (reference state). [e] Ethylene, twisted by 90°, open-shell SCF for triplet. [f] Energy difference between the s-trans planar structure and the conformer twisted by 90° around the C-C single bond. All bond lengths and valence angles were assumed to have ihe same values in the two conformers (C-C 1.48 Å).

theories, the values have to be corrected for compression energies of the σ bonds, since the σ bonds in the conjugated system are supposed to be shortened owing to the π contribution of the conjugated double bonds. Since in our calculations all electrons are included, we can compute directly the adiabatic resonance energy by optimizing the CC single bond length with respect to the energy expectation value referring to the reference state without conjugation. The SCF energy and the energy of the reference state without resonance are depicted in Figure 1 for butadiene calculated with DZ + D. The vertical resonance energy is decreasing with increasing C-C single bond distance. Thus, the minimum of the energy curve of the reference state appears at a (~0.05 Å) longer C-C distance than the minimum of the SCF energy and the adiabatic resonance energy is slightly smaller than the vertical resonance energy. For comparison the length of the sp^2-sp^2 single bond in twisted ethylene (triplet[25]) is also given in Table I. This bond is about 0.05 Å shorter than the single bond in the reference state of butadiene. Obviously, the nonresonating double bond orbitals repel each other more strongly than do normal vicinal σ bond orbitals. The same is known of the repulsion of lone pairs. The repulsion of the nonresonating double bonds is also reflected in the values calculated for the resonance energy of butadiene, which are considerably higher than any experimental estimate of the resonance energy and also higher than the computed rotational barrier of the C-C single bond in butadiene which is also given in Table I. Thus, the coplanar arrangement is no longer the most favorable for a butadiene with nonresonating double bonds. This is in accordance with the observation that β substituents stagger rather than eclipse a double-bond orbital.[26] The conformational preferences in compounds like propene, 1-butene, and 2-butene (cf. ref 26) prove that hyperconjugation between the double bond MO and the vicinal σ bond orbital cannot compensate for this type of repulsion. The conjugation of the double bonds, on the other hand, overcompensates the repulsion of the eclipsed π MOs and even gives some extra stability to the molecule which can be attributed to a thermochemical resonance energy of some 3 kcal/mol.[2] One might also say that the standard additive relationship for heats of formation does not hold for the nonresonating model hydrocarbon because of a destabilization due to the repulsion of the nonresonating double bonds.

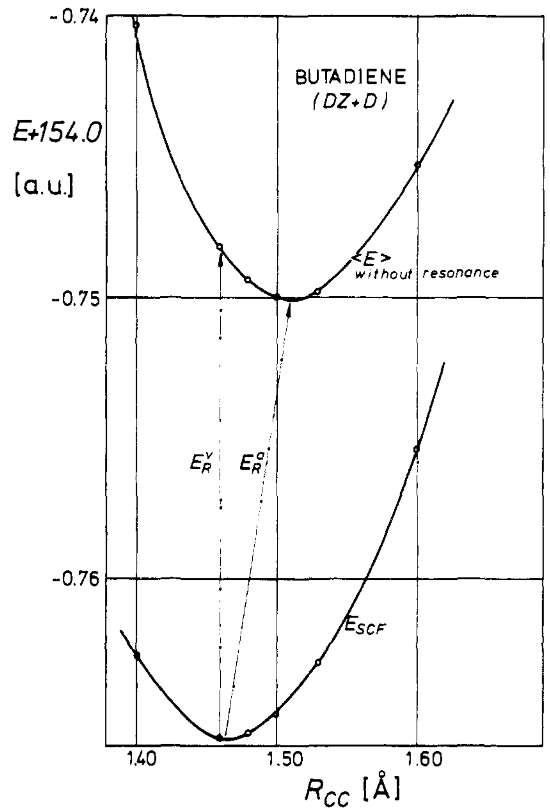


Figure 1. The SCF energy and the energy of the reference state of butadiene as a function of the C-C single bond distance (C=C 1.34 Å; DZ + D basis).

4. Influence of Correlation on the Resonance Energy. The electrons of the two π orbital electron pairs are packed slightly more densely in the strictly localized π MOs of the model wave function than they are in the SCF π orbitals of butadiene. Hence, electron correlation is expected to contribute more to the reference state than to the ground state of butadiene.

When only the π electron correlation energy is calculated, correlation will favor the reference state over the ground state by about 1.1 kcal/mol in the DZ + D basis. The value is reduced to 0.7 kcal/mol when the total correlation energy of the carbon skeleton is taken into account, since the delocalized π MOs have slightly larger interorbital correlation energy contributions with the σ MOs than have the strictly localized π MOs. The effect of electron correlation on the computed resonance energy is overestimated with the smaller basis sets. The minimal basis allows for right-left correlation only. This type of correlation is affected most by the change in the wave function when going from conjugating to nonconjugating π MOs. The angular correlation which can only be described in a basis containing d orbitals is much less affected.

It is concluded that electron correlation reduces the calculated vertical resonance energy of butadiene by less than 10%. For an estimation of this correlation effect one needs rather large basis sets.

VI. Benzene

Resonance in benzene (**9**) is an important factor responsible for its thermochemical stability and its structure with six CC bonds of identical length. For the vertical resonance energy, a value of 86 kcal/mol was obtained with the DZ basis (Table II). Strictly localized ethylene π MOs are very different from the delocalized SCF π MOs of benzene. Thus, the electron correlation in the π system increases considerably when going from SCF to nonresonating model π MOs. The difference in

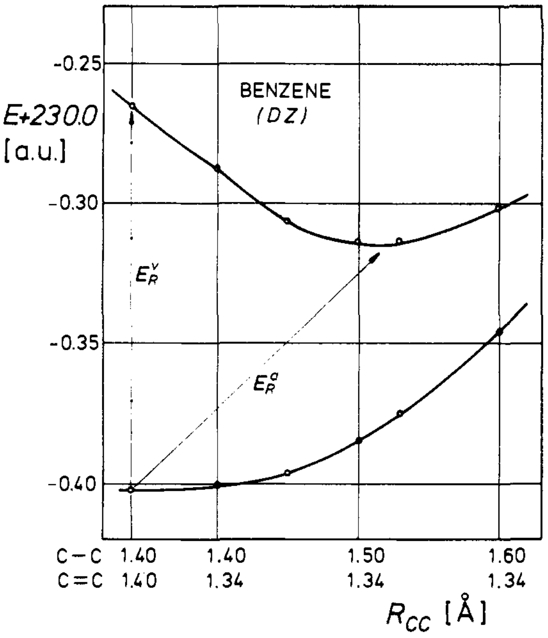


Figure 2. The SCF energy and the energy of the reference state of benzene as a function of the CC bond distances (DZ basis).

π electron correlation is partly offset by the σ-π interpair correlation energy contributions which favor the wave function with delocalized π MOs. In total, the vertical resonance energy of benzene is reduced by about 9 kcal/mol (DZ) to 77 kcal/mol when correlation is taken into account. The large change in the π system when going from the SCF π MOs to the nonresonating π MOs has still a very small effect on the σ system. The optimization of the σ orbitals with the frozen model π MOs lowers the energy expectation value—and thus, the vertical resonance energy—only by about 1.2 kcal/mol.

Obviously, the geometrical structure of benzene with six identical CC bonds of 1.40 Å is no longer appropriate for the reference state with three π MOs belonging to three localized π bonds. The optimum structure **10** of the reference state has alternate bonds with a single bond length of 1.51 Å (DZ) which is only slightly longer than the corresponding C-C bond in butadiene. The energy expectation value for the optimum structure is 30 kcal/mol lower than for the D_{6h} structure (Figure 2). Thus, the adiabatic and the vertical resonance energies of benzene differ much more than in the case of butadiene. The adiabatic resonance energy of benzene is computed to be 56 kcal/mol (DZ). With inclusion of correlation, the value is reduced to 50 kcal/mol.

It is noteworthy that the vertical resonance energy of a "cyclohexatriene" **10** with alternate bonds of 1.34 and 1.48 Å is still about 50 kcal/mol and thus more than five times as large as the vertical resonance energy of butadiene with the same bond lengths. Thus, the relatively small difference between the total SCF energies of the systems **9** and **10** of about 8 kcal/mol is by no means an indicator for the resonance energy of benzene.

In Table II all values are given for two basis sets, the MB and the DZ basis. The differences between the two basis sets are never large and show the same trends as in the case of butadiene. Hence, for larger molecules, we can safely use the MB remembering its tendency to slightly overestimate resonance energies.

As in the case of butadiene, we have to note that part of the calculated resonance energy of benzene is used up in compensating the unfavorable repulsion between the localized π bonds. Though we cannot say anything about the size of that repulsion, we may well assume that the repulsion of two strictly localized π orbitals in benzene and in butadiene will be the same when the same bond lengths are used. The extra stabilization of benzene as compared to butadiene is the normalized resonance energy defined according to eq 1.

Table II. Resonance Energy of Benzene (kcal/mol)

	MB	DZ
total SCF energy[a,b]	228.3062	230.4029
vertical resonance energy (SCF)	95.8	96.4
contribution of σ relaxation	−0.4	−1.2
contribution of correlation π only	−20.7	−16.0
total[c]	−13.1	−9.1
adiabatic resonance energy (SCF)	58.5	56.0
contribution of σ relaxation	−0.1	−0.2
contribution of correlation[c]	−9.7	−6.4
optimum C-C bond lengths[d]	1.527	1.510
normalized resonance energy with SCF	32.4	28.2
with correlation included	26.0	25.7

[a] Bond lengths: CC 1.40 Å, CH 1.10 Å. [b] Total SCF energy in au. [c] All electron pairs of the CC skeleton (9 MOs, 81 electron pairs) included. [d] Optimum C—C bond length in the reference state with nonconjugating π MOs transferred from ethylene (σ optimization and correlation not included); C=C assumed to be 1.34 Å.

Table III. Relative Energies[a] of the Reference States of Naphthalene

		naphthalene[b]	distorted naphthalenes[c]	
		16	**17**	**18**
SCF		0	13	21
ref state	**17**	167	95	
	18	170		96

[a] Energies in kcal/mol relative to the SCF energy of naphthalene. [b] CC bond lengths 1.40 Å. [c] CC single bonds 1.52 Å, double bonds 1.34 Å.

As normalized resonance energies we obtain for benzene 28 kcal/mol with SCF and 26 kcal/mol with inclusion of correlation. These values, which were obtained from a purely theoretical calculation of the effect of the localization of π electrons, compare surprisingly well with thermochemical estimates for the resonance energy. It clearly demonstrates the value of the thermochemical model which basically assumes an additive scheme for the heats of formation of molecules and assigns all deviations from the additive scheme to certain effects present in the molecule, like resonance, ring strain, etc.

VII. Naphthalene and Azulene

For naphthalene (**16**) two nonequivalent valence structures **17** and **18** can be written. As the results of Table III show, the energy difference between the corresponding adiabatic reference states is small and the adiabatic resonance energy of naphthalene with respect to structure **17** comes out to be 95 kcal/mol. With the normalization described before, a value for the resonance energy of naphthalene of 43 kcal/mol is obtained. As in the case of benzene the SCF value is somewhat above the experimental estimates (39 kcal/mol from Wheland[2] and 30.5 kcal/mol from Dewar[6]). However, inclusion of electron correlation is expected to reduce the computed resonance energy. The naphthalene system is too large for a calculation of the effect of electron correlation. One might expect a partial cancellation of the correlation effects when only the extra stabilization of naphthalene with respect to the benzene and the butadiene subunits is considered. For this extra stabilization of the π system of naphthalene a value of 10.5 kcal/mol is computed which compares much better with the experimental values of 13.5 kcal/mol of Wheland[2] and 10.5 kcal/mol of Dewar.[6]

Azulene (**19**) is an isomer of naphthalene. Thermochemically, **19** is about 37.4 kcal/mol less stable than naphthalene.[27] Because of its nonalternant π system it has a considerable dipole moment of 1.08 D.[28] The dipole moment has been attributed to the partial negative charge in the five-membered ring and the partial positive charge in the seven-membered ring arising from the cross conjugation of the two rings.[29] π theories yield very large dipole moments of above 2 D.[30]

For a structure with identical bond lengths of 1.40 Å along the perimeter (1.48 Å for the bond common to the two rings) we computed a SCF dipole moment of 1.89 D and a vertical resonance energy of 132 kcal/mol, which is 34 kcal/mol less than in the case of naphthalene. The reference state with π MOs transferred from ethylene has a dipole moment of 0.23 D with the sign reversed. By optimization of the σ orbitals in the reference state with frozen π MOs 2.0 kcal/mol is gained and the dipole moment is not more than 0.03 D (original direction). Thus, the dipole moment of azulene arises from the π system only. The underlying σ system is polarized in the opposite direction. The contribution of σ orbital relaxation to the resonance energy is small though no longer negligible.

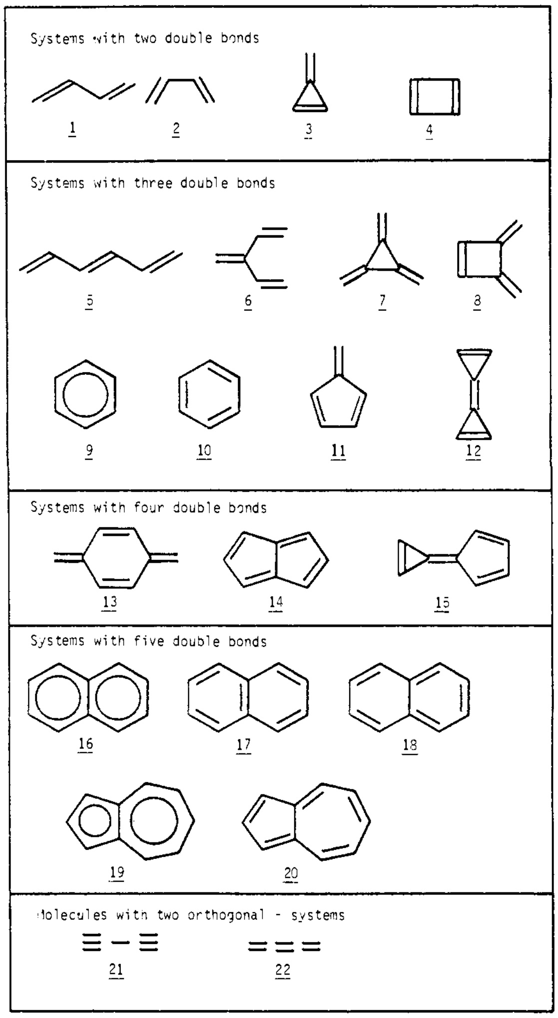
From a calculation on the structure **20**, which is more appropriate for the reference state and which contains alternate bonds on the perimeter of 1.34 and 1.52 Å, a value of 66.0 kcal/mol is computed for the adiabatic resonance energy of azulene. The difference between the adiabatic resonance energies of naphthalene and of azulene is 29 kcal/mol, leaving a normalized resonance energy of 14 kcal/mol for azulene.

The dipole moment calculated for **20** (0.95 D) agrees surprisingly well with experiment (1.08 D). In other cases dipole moments are underestimated by MB SCF calculations, since the MB has not enough flexibility to allow for larger charge transfers. Examples are fulvene (dipole moment 0.67 D with MB SCF; experimental 1.1 D[23] and methylenecyclopropene (SCF dipole moment, MB 2.06 D, DZ 2.10 D; DZ + D 2.25 D; cf. section IX). The C_{2v} structure **19** for azulene with nonalternate bonds can hardly be reconciled with the small experimental dipole moment. In fact, the experimental structure of azulene is not well-known.[31] MINDO/3[32] calculations favored the C_{2h} structure with alternate bond lengths slightly (by 1.6 kcal/mol) over the C_{2v} structure.[16] There are other semiempirical calculations of a geometry optimization of azulene in which, however, C_{2v} symmetry was assumed.[34] No bond alternation for azulene was predicted by a π theoretical study.[35] Ab initio calculations on azulene[33] were also based on a C_{2v} structure.

The SCF energy of structure **20** with perimeter bond lengths of 1.34 and 1.52 Å is 7.1 kcal/mol above the SCF energy of **19** with 1.40 Å as the perimeter bond distance. For naphthalene the corresponding SCF energy differences are 13.1 and 19.4 kcal/mol for structures **17** and **18**, respectively. However, no geometrical parameters were optimized in these calculations. Next we performed MB SCF calculations on the optimum structures with C_{2v} and with C_{2h} symmetry as obtained by MINDO/3. In both cases the SCF energies were lower than before. The energy difference between the two structures was computed to be 3.0 kcal/mol with the C_{2h} structure **20** having now the lower energy. According to the MB SCF energies, **20** is 48.8 kcal/mol above **16**. The SCF dipole moments are 1.92 and 1.40 D for the MINDO/3 optima with C_{2v} and C_{2h} symmetry, respectively. Though the energy difference computed with MB SCF should be taken with care, the computed dipole moments are strong indicators for a structure with bond distances which might be even more strongly alternating than predicted by MINDO/3 (C=C between 1.36 and 1.39 Å; C—C between 1.45 and 1.49 Å along the perimeter).

Concerning the resonance energy, it is then probably more correct to consider structure **20** rather than **19**. Taking standard bond lengths of 1.48 and 1.34 Å for the perimeter (SCF dipole moment 1.05 D), a vertical resonance energy of 66.2 kcal/mol (0.6 kcal/mol for σ relaxation included) is obtained which gives a normalized value of 8.5 kcal/mol as the resonance energy of azulene (cf. Table III and section VIII). The major part of the energy difference between azulene and naphthalene has to be attributed to the less favorable π system of the former rather than to ring strain. Though azulene has probably a structure with alternate bond lengths, resonance in the π system gives the molecule more stability than would be predicted for a normal conjugated hydrocarbon.

Chart I. π Systems for Which Resonance Energies Have Been Computed



VIII. Nonaromatic Conjugated Hydrocarbons

For the study of resonance energies of nonaromatic conjugated hydrocarbons MB was used throughout. In addition, it seemed sufficient to compute the vertical resonance energies for given bond lengths of 1.34 and 1.43 Å. The normalization of the vertical resonance energies with respect to the vertical resonance energy of butadiene should give essentially the same result as the normalization of the adiabatic resonance energies with respect to the adiabatic resonance energy of butadiene, since the energy contribution of the relaxation of the single bond lengths per single bond is expected to be the same in butadiene and in other nonaromatic hydrocarbons.

The results for several conjugated hydrocarbons are summarized in Table IV. The vertical resonance energies depend considerably on the type of conjugation. While the resonance energy of three conjugated double bonds is about 20 kcal/mol

Table IV. Resonance Energies of Nonaromatic Conjugated Hydrocarbons[a]

no. in Chart I	name	vertical resonance energy[b]	normalized resonance energy	PPP resonance energies[c]
1	butadiene	9.7	0.0	0.1
2	*s-cis*-butadiene	8.7	−1.0	0.8[d]
3	methylenecyclopropene	23.2	3.8	
4	cyclobutadiene	0.0	−19.4	−18.0
5	hexatriene	20.4	−1.0	0.0
6	2-vinylbutadiene	18.1	−1.3	−0.6
7	3-radialene	25.9	−3.2	~0
8	dimethylenecyclobutene	26.4	−2.7	
10	"cyclohexatriene"	52.4	23.3	20.0[e]
11	fulvene	29.8	0.7	1.1
12	triafulvalene	37.8	−1.0	
13	1,3-benzenequinododimethide	40.4	1.6	
14	pentalene	45.6	−2.9	0.1
15	calicene	59.2	10.7	1.5
17		98.3	40.1	30.5[e]
18		91.3	33.1	
20	azulene[f]	66.8	9.1	3.9

[a] Values in kcal/mol for minimal basis. Bond lengths used throughout: C=C 1.54 Å, C—C 1.48 Å, C—H 1.10 Å. [b] Without σ relaxation, correlation not included. [c] Values from ref 7d; value for calicene from ref 7b. [d] When nonbonded σ orbital interactions are taken into account, **2** is predicted to be less stable than **1**.[7e] [e] For nonalternant bond lengths. [f] The bond shared by the two rings was assumed to be 1.52 Å.

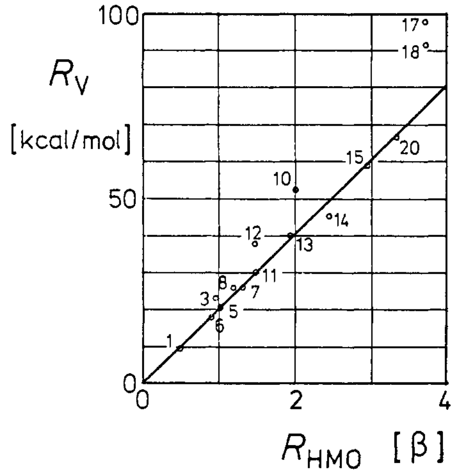


Figure 3. Vertical ab initio resonance energies of conjugated hydrocarbons (numbering of Chart I) vs. Hückel resonance energies.

in hexatriene (**5**), it assumes a value of 38 kcal/mol in triafulvalene (**12**). However, the latter system contains four single bonds connecting the double bonds compared to only two single bonds in hexatriene. Thus, the normalized resonance energies of hexatriene and of triafulvalene differ by less than 2 kcal/mol with the hexatriene having the energetically more favorable π system.

Even though very different types of conjugative π systems are represented by the hydrocarbons listed in Table IV, the nonaromatic systems have all very small normalized resonance energies which do not exceed about 1 kcal/mol per double bond with the notable exceptions of methylenecyclopropene (**3**) and of calicene (**15**), which are discussed in section IX. Our normalized resonance energies are in satisfactory agreement with Dewar's PPP resonance energies.[7]

As Figure 3 shows, vertical ab initio resonance energies and Hückel resonance energies are proportional to each other with a proportionality constant of 20 kcal/mol·β.[1] This result is surprising in view of the large π bond orders calculated within the Hückel theory for single bonds. Deviations occur mainly for aromatic systems where π bond orders are large also within ab initio. The proportionality of Figure 3 can be considered as a theoretical justification for the normalization of Hückel resonance energies. One needs fairly complicated normalization schemes[14] in order to accommodate those systems which show larger deviations from the proportionality relationship.

IX. Nonalternant Hydrocarbons

The nonalternant π system of fulvene (**11**) is polarized with a partial negative charge in the aromatic five-membered ring. The experimental dipole moment is 1.1 D.[28] SCF calculations yield dipole moments of 0.67 and 0.77 D with the MB and DZ basis sets, respectively. When the SCF π orbitals are replaced by strictly localized nonpolar π orbitals transferred from ethylene, the dipole moment reverses its sign and decreases in magnitude to 0.22 and 0.28 D for the two basis sets. The π MOs of fulvene have polarized the σ system somewhat in the opposite direction. Relaxation of the σ MOs in the reference state with frozen nonpolar π MOs leads to a further reduction of the dipole moment to about 0.1 D (original direction) for both basis sets. Thus, after elimination of resonance the reference state represents a completely nonpolar hydrocarbon system.

The normalized adiabatic resonance energy of fulvene comes out to be −2.5 and −1.5 kcal/mol for MB and for DZ, respectively. These values include the contributions of the relaxation of the σ MOs in the reference state (0.4 kcal/mol with MB and 0.5 kcal/mol with DZ). The main effect of resonance in **11** is a considerable charge transfer which is not connected with any stabilization of the molecule.

The π system in methylenecyclopropene (**3**) is more strongly polarized than in fulvene. The three-membered ring bears a partial positive charge. Ab initio SCF calculations performed on this molecule have given a very large dipole moment and unusually short C-C single bond lengths of 1.44 Å on the STO-3G level.[26] The molecule is small enough to allow computations even with the DZ + D basis. The results are summarized in Table V. According to the calculations with the DZ + D basis, methylenecyclopropene has very short single bonds of 1.42 Å only.

In SCF we compute a dipole moment of 2.25 D with the DZ + D basis. When the π MOs in the wave function are replaced by strictly localized π MOs transferred from ethylene, the dipole moment almost vanishes (0.19 D) while reversing its

Table V. Resonance in Methylenecyclopropane (Energies in kcal/mol; Distances in Å)

	MB	DZ	DZ + D
SCF energy[a,b]	152.0336	153.4463	153.5257
dipole moment[a,c]	−2.06	−2.10	−2.25
ref state method 3:[d] vertical resonance energy	26.4	26.3	30.8
dipole moment[c,e]	−0.79	−0.77	−0.97
contribution of σ relaxation	−1.3	−1.5	−1.7
dipole moment[c,f]	−1.18	−1.24	−1.43
ref state of method 1[g]; vertical resonance energy	26.9	27.5	
dipole moment[c,e]	+0.19	+0.19	
contribution of σ relaxation	−1.8	−1.7	
dipole moment[a,f]	−0.25	−0.36	
optimum C-C lengths, SCF	1.487	1.450	1.427
ref state[d,h]	1.524	1.512	1.494
adiabatic resonance energy[h]	21.3	21.3	26.8
normalized adiabatic resonance energy[h]	3.9	2.7	7.4

[a] C=C 1.34 Å, C—C 1.44 Å. [b] Total energy in au. [c] In debye. Negative sign: partial positive charge in the three-membered ring. [d] The π MOs in the model wave function were obtained from the SCF π MOs by localization according to Boys and truncation. [e] Dipole moment of the reference state. [f] Dipole moment of the reference state, σ relaxation included. [g] With π MOs transferred from ethylene. [h] σ relaxation included.

sign. That is in principle the same behavior as in the cases of fulvene and of azulene, though in the present case the polarization of the σ system is remarkably small in view of the large charge transfer in the π system. Relaxation of the σ orbitals in the reference state with the frozen nonconjugating π MOs leads quite unexpectedly to an increase of the dipole moment with reversal of sign again indicating a partial positive charge in the three-membered ring. The energy lowering connected with the σ orbital relaxation amounts to 1.8 and 1.7 kcal/mol for MB and for DZ, respectively, which is about three to four times as much as in the case of fulvene.

As it turned out, the ethylene-type nonpolar π MOs are not the most favorable nonresonating π MOs for the reference state of **3**. When the two SCF π MOs of methylenecyclopropene are subjected to a Boys localization and are then truncated and reorthogonalized (method 3, section III) an energy expectation value is obtained which is about 0.7 kcal/mol (DZ) lower than the energy of the reference state with the ethylene π MOs. We determined also the optimum nonresonating π MOs. They are somewhat less polarized; the energy gain compared with the truncated localized π MOs is negligible (~0.1 kcal/mol). The dipole moment of the reference state of methylenecyclopropane with the optimum nonresonating π MOs and with optimized σ MOs is still about 1 D, with the σ and the π contributions having about the same weight. It is known that cyclopropene itself has a fairly large dipole moment of 0.46 D.[28]

The normalized adiabatic resonance energy of **3** is unexpectedly large. With the DZ + D basis a value of 8 kcal/mol is obtained (3 kcal/mol with DZ). The d orbitals in the basis seem to enhance the conjugation. Part of this effect has to be attributed to the shorter C-C bond distance in the case of the DZ + D basis.

In calicene (**15**) we find the π systems of **3** and of **11** combined. The MB SCF dipole moment of 4.16 D (bond lengths 1.34 and 1.48 Å) indicates a large charge transfer from the three-membered to the five-membered ring. The reference state with ethylene π MOs has a dipole moment of 0.45 D in the opposite direction. Relaxation of the σ orbitals in the reference state lowers the energy by 3.0 kcal/mol and reduces the dipole moment to 0.12 D (original direction). Boys localization and truncation of the SCF π MOs leads to a reference state with the same energy (within 0.01 kcal/mol) as that of the reference state with ethylene π MOs. The dipole moment would then be 1.07 D. The normalized resonance energy of **15** is calculated to be 10.7 kcal/mol (with σ orbital relaxation included). This is an unusually large value for a nonaromatic hydrocarbon which is in disagreement with PPP theoretical estimates.[7b]

Table VI. Resonance Energies of Butadiyne and of Butatriene (DZ + D Basis; kcal/mol)

	butadiyne[a]	butatriene[b]
total SCF energy, au	152.3763	153.5509
optimum C-C bond length, Å	1.384	1.257
vertical resonance energy	22.3	20.5
contribution of σ relaxation	−0.2	−0.3
adiabatic resonance energy	19.1	18.9
optimum C-C bond length, Å[c]	1.458	1.296

[a] C≡C 1.20 Å, C—H 1.06 Å assumed. [b] Outer C=C 1.33 Å, CH 1.08 Å assumed. [c] Refers to the reference state without conjugation.

X. Molecules with Two Orthogonal π Systems

Butadiyne (**21**) has two orthogonal π systems of the butadiene type. The vertical resonance energies of the two systems are almost additive. The removal of resonance in one of the π systems leads to an energy increase which amounts to 49.7% of the energy increase computed for the removal of resonance in both π systems. The vertical resonance energy of one π system in butadiyne of 10.4 kcal/mol (Table VI) is considerably smaller than the vertical resonance energy of butadiene (14.1 kcal/mol) when the same C-C single bond length of 1.40 Å is used for both molecules. The single bond in butadiyne is very short (1.384 Å in SCF, DZ + D; experimental value 1.376 Å[36]). Cutting off the conjugation in both π systems lengthens the single bond by 0.07 Å to 1.457 Å, a value which is still much smaller than the bond length of a normal C-C single bond. Thus, butadiyne owes its very short single bond to two factors, sp hybridization and resonance in the π system. Because of the short single bond, the total adiabatic resonance energy of butadiyne is 19 kcal/mol, almost double that in butadiene (9.7 kcal/mol).

In butatriene (**22**) the central bond is a double bond and therefore even shorter than the central bond of butadiyne. Thus, the adiabatic resonance energy of the butadiene-like π system in butatriene is almost twice as large as in butadiene. The optimum double bond in the reference state without conjugation is still slightly shorter than the double bond of ethylene (1.310 Å with the same basis; compared to experiment double bonds are too short within SCF).

For both molecules, the computed resonance energies cannot be compared with experimental quantities, since the reference energies of a sp-sp hybridized CC single and double bond without conjugation cannot be obtained.

XI. Conclusions

We have calculated resonance energies for numerous conjugated hydrocarbons directly by making use of a model wave function for a reference state without conjugation. The results have shown that the energy gained from the delocalization of π electrons is unexpectedly large. Part of that purely theoretical resonance energy is used up for compensating the unfavorable repulsion of eclipsed π MOs. Comparison of the theoretical resonance energies with the corresponding thermochemical data has been enabled by a normalization of the computed resonance energies with respect to butadiene.

Our direct calculation of a resonance energy includes the effort of a full ab initio SCF calculation of the molecule considered. One could, of course, use the SCF energy itself for drawing conclusions about the stability of the molecule. In addition, one could compute theoretically the enthalpy changes of isodesmic and of homodesmotic reactions in order to deduce resonance energies defined in the same way as the experimental resonance energies. This would, however, still not answer the conceptually interesting question: which part of the stability of a molecule can be attributed to the resonance in the π system? Moreover, resonance energies directly calculated from model wave functions are expected to depend less on the basis set and less on the details of the structural parameters, like valence angles and CH bond lengths, than the total SCF energy. Since larger π systems can only be calculated within minimal basis sets, the total SCF energy has not much meaning and is certainly less accurate than a directly computed resonance energy.

The principle of calculating an energy expectation value with respect to a model wave function can as well be applied to other terms used in chemistry which are based on certain models, like hyperconjugation, inductive effects, etc. In the analysis of molecular interactions (hydrogen bonds, certain regions of a potential energy surface of a chemical reaction) reference states containing the molecular orbitals of unperturbed subsystems could be of some interest.

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In Situ Resonance Raman Spectroscopic Investigation of the Tetrathiafulvalene–Tetracyanoquinodimethane Electrode Surface

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Abstract: Resonance Raman spectroscopy was applied to the study of the tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) electrode in an aqueous 1.0 M KBr solution and spectroscopic evidence is presented which shows that oxidative decomposition of the electrode results in the formation of neutral TCNQ. Subsequent waves for surface processes in the cyclic voltammetry of the oxidized TTF–TCNQ electrode can be directly attributed to the reduction of electrogenerated TCNQ and reoxidation of the reduced product (KTCNQ) by simultaneously monitoring the current and the Raman intensity of the strongest neutral TCNQ band as a function of applied potential.

The in situ characterization of heterogeneous electron transfer reactions occurring at the electrode–solution interface by the techniques of normal and resonance Raman spectroscopy has been shown to be feasible and highly informative. To date several studies have been reported characterizing (1) stable electrogenerated species produced by exhaustive electrolysis and monitored under steady-state conditions in the bulk solution;[1] (2) transient species generated in the electrochemical diffusion layer;[2] (3) species undergoing potential-controlled adsorption on metal and semiconductor electrodes;[3,4] (4)

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