Tetrahedron. Vol. 32, pp. 205 to 209 Pergamon Press 1976. Printed in Great Britain

WHY IS AZULENE BLUE AND ANTHRACENE WHITE? A SIMPLE MO PICTURE

J. MICHL* and E. W. THULSTRUP†
Department of Chemistry, University of Utah, Salt Lake City, UT 84112, U.S.A.

(*Received in USA* 21 *March* 1975; *Received in UK for publication* 7 *July* 1975)

Abstract—In spite of their almost identical ionization potentials (IP's) and electron affinities (EA's), azulene and anthracene differ considerably in their lowest singlet-singlet excitation energies. This is hard to understand in the simple Hückel picture in which excitation energies are expressed as orbital energy differences, if orbital energies are taken from IP's and EA's. The difficulty is removed when electron repulsion is introduced explicitly. This is shown using simple intuitive concepts, which also account for the magnitude of singlet–triplet splitting and single out the structural features responsible for the difference between azulene and anthracene, so that generalizations are possible.

INTRODUCTION

Simple MO theory at the Hückel level provides the organic chemist with a useful picture of phenomena related to electronic excitation. According to this theory, the first ionization potential of a molecule is equal to minus the energy of the highest occupied MO (HOMO); the first electron affinity of a molecule is equal to minus the energy of the lowest unoccupied MO (LUMO), and the excitation energy of the lowest electronic transition, corresponding to the HOMO→LUMO jump, is related to the HOMO–LUMO energy difference. Naively, one might expect the excitation energy to be equal to the orbital energy difference, but it has been known for some time[1-3] that this is not so. The linear correlation between excitation energies of the singlet L_a band (Clar's p-band) of alternant hydrocarbons (conjugated hydrocarbons with no odd-membered rings), which corresponds to HOMO→LUMO excitation, and the Hückel orbital energy differences does not pass through the origin.[1-3] Moreover, points for some non-alternant hydrocarbons, e.g. azulene (1), lie far off the regression line, while those for others, e.g. fluoranthene (2), do not.[4] The situation is illustrated in the first four columns of Table 1. Clearly, the fact that azulene and anthracene (3) have almost identical ionization potentials and electron affinities, suggesting similar HOMO and LUMO energies for the two hydrocarbons, is hard to reconcile with the fact that one (1) is blue and the other one (3) white (in both cases, the longest wavelength singlet-singlet absorption band, which determines the color, is due to HOMO→LUMO excitation).

The purpose of the present article is to show how this apparent paradox is removed at the next higher level of approximation, which is still quite simple and easy to visualize in pictorial terms, and how the difference between 1 and 3 can be simply rationalized in terms of molecular structure and of shapes of Hückel molecular orbitals.

Electron repulsion integrals. The step which needs to be taken in order to remove the above-mentioned discrepan-

Table 1*

	$I.P._{.1}$	$E.A._{.-1}$	$T_{1\to-1}$	$S_{1\to-1}$	$-J_{1,-1}+2K_{1,-1}$	$J_{1,-1}$	$2K_{1,-1}$
Naphthalene (4)	8·2[b]	0·2[c]	2·6[d]	4·3[d]	−3·7	5·4	1·7
Anthracene (3)	7·4[b]	0·6[c]	1·8[d]	3·3[d]	−3·5	5·0	1·5
Azulene (1)	7·4[e]	0·7[c]	1·3[f]	1·8[d]	−4·9	5·4	0·5

*Experimental values of ionization potential ($I.P._{.1}$), electron affinity ($E.A._{.-1}$), and triplet and singlet transition energies ($T_{1\to-1}$, $S_{1\to-1}$), where HOMO is indicated by 1 and LUMO by −1. Electron affinities are in general not known very precisely, but relative values are probably reliable for the molecules included. The values for $-J_{1,-1}+2K_{1,-1}$, $J_{1,-1}$ and $2K_{1,-1}$ have been determined from the experimental numbers according to:

$$-J_{1,-1}+2K_{1,-1} = -I.P._{.1}+E.A._{.-1}+S_{1\to-1}$$

$$J_{1,-1} = I.P._{.1}-E.A._{.-1}-T_{1\to-1}$$

$$2K_{1,-1} = S_{1\to-1}-T_{1\to-1}$$

All quantities are given in eV.

[b]P. A. Clark, F. Brogli and E. Heilbronner, *Helv. Chim. Acta* **55**, 1415 (1972).

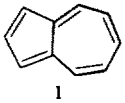
[c]R. S. Becker and E. Chen, *J. Chem. Phys.* **45**, 2403 (1966).

[d]J. B. Birks, *Photophysics of Aromatic Molecules*. Wiley-Interscience, New York (1970).

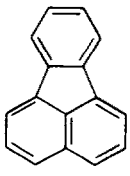
[e]R. H. Huebner, W. F. Frey and R. N. Compton, *Chem. Phys. Lett.* **23**, 587 (1973).

[f]P. M. Rentzepis, *Ibid.* **3**, 717 (1969).

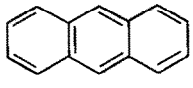
†Permanent address: Department of Chemistry, Aarhus University, DK-8000 Aarhus C, Denmark.



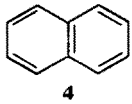
1



2



3



4

cies is explicit introduction of average electron repulsion. This is achieved in the self-consistent-field (SCF) model, in which an orbital energy corresponds to the energy of an electron which feels the field of the nuclei as well as time-averaged fields of the other electrons. Since only time-averaged effects are considered, one would expect that the mutual repulsion of two electrons 1 and 2 in two orbitals ψ_a and ψ_b is given by the classical electrostatic repulsion energy of the two charge distributions, $\psi_a^2(1)$ and $\psi_b^2(2)$. Using Coulomb's law, this can be expressed as an integral over all three spatial coordinates of each electron, x_1, y_1, z_1 and x_2, y_2, z_2, the so-called Coulomb integral $J_{a,b} = \int\int\int\int\int\int \psi_a^2(1)(e^2/r_{12})\psi_b^2(2)\ dx_1dy_1dz_1dx_2dy_2dz_2$, where $r_{12} = \sqrt{[(x_1-x_2)^2+(y_1-y_2)^2+(z_1-z_2)^2]}$.

However, this is only true if the two electrons have opposite spin. If they have like spins, the time-averaged energy of their repulsion is not $J_{a,b}$, but only $J_{a,b} - K_{a,b}$, where $K_{a,b}$ is called the exchange integral. It corresponds to the electrostatic interaction between an overlap charge density $\psi_a(1).\psi_b(1)$ due to electron 1 and the same charge density $\psi_a(2).\psi_b(2)$ due to electron 2: $K_{a,b} = \int\int\int\int\int\int \psi_a(1)\psi_b(1)(e^2/r_{12})\psi_a(2)\psi_b(2)\ dx_1dy_1dz_1dx_2dy_2dz_2$. Unlike "real" charge densities $\psi^2(1)$, which are necessarily positive or zero, overlap charge densities $\psi_a(1)\psi_b(1)$ can be positive in some regions of space and negative in others, depending on the relative signs of $\psi_a(1)$ and $\psi_b(1)$. Electrostatic interaction of overlap densities $\psi_a(1)\psi_b(1)$ and $\psi_a(2)\psi_b(2)$ is thus composed of repulsion between regions of charges of like sign, as well as attraction between regions of unlike sign, but it can be shown that attraction can never dominate, i.e. $K_{a,b} \geq 0$.

The physical reason behind the reduced repulsion of two electrons with parallel spins can be seen in the decreased probability with which they come near each other as a result of the Pauli exclusion principle,[5] but more detailed analysis indicates that the situation is actually quite complicated.[6]

Relation of excitation to ionization and electron capture. We are now ready to keep proper track of changes in electron repulsion energies during the processes of ionization, electron capture and excitation of an ordinary (closed shell) organic molecule at the level of simple SCF theory. The first ionization potential still corresponds to minus the SCF energy of HOMO and the first electron affinity to minus the SCF energy of LUMO (Koopmans' theorem[7]). In order to derive expressions for singlet and triplet HOMO→LUMO excitation energies it is instructive to separate excitation into two steps. The first one corresponds to removal of an electron from HOMO to infinity and requires energy equal to the first ionization potential ($-\epsilon_{HOMO}$). In the second step, the electron is brought back and placed in LUMO. If the first step had not taken place, this would release an amount of energy equal to the first electron affinity of the neutral molecule ($-\epsilon_{LUMO}$). The total energy required for the excitation would then be $-(\epsilon_{HOMO} - \epsilon_{LUMO})$, i.e. the first ionization potential minus the first electron affinity. However, the first step had, of course, been performed, so that a hole is present in HOMO while the electron is being brought back from infinity. One electron repulsion contribution will thus be missing, and this will facilitate the delivery of the electron from infinity to LUMO. The amount of energy saved will be just $J_{HOMO,LUMO}$ or $J_{HOMO,LUMO} - K_{HOMO,LUMO}$, depending on whether the repulsion term which is no longer present would have been between two electrons of opposite spin ($J_{a,b}$) or of like spin ($J_{a,b} - K_{a,b}$). In the former case, one ends up with a triplet excited state, since the electron which remained in HOMO and the one which has now been placed in LUMO have the same spin. Depending on whether this is up or down, we end up with one or a second of the three isoenergetic components of the triplet state (Fig. 1). In this approximation, the excitation energy for the HOMO→LUMO triplet excitation thus is $-(\epsilon_{HOMO} - \epsilon_{LUMO}) - J_{HOMO,LUMO}$ (i.e. the difference of the ionization potential and electron affinity minus the Coulomb integral).

One may now wonder what happened to the third component of the triplet state. Unlike the previous two, which had the total spin angular momentum pointing up or down (more accurately, a positive or negative projection of this moment into the z-axis), the third one has its total spin angular momentum pointing sideways and its projection along the z-axis vanishes, just like that of the singlet state. As a matter of fact, both this third component of the triplet state and the singlet excited state result from the other mode of performing the second step in our stepwise generation of excited states, namely the one in which the electron being brought back from infinity to LUMO has the same spin as the one which had been removed from HOMO, i.e. the opposite spin than the electron which had remained behind in HOMO. The amount of energy saved now is only $J_{HOMO,LUMO} - K_{HOMO,LUMO}$. Since the production of the triplets actually gave two states depending on whether the total spin pointed up or down, it is hardly surprising that the present attempt to produce a singlet also produces two states, since one or the other electron can have its spin up, giving two independent wavefunctions of energy equal to $-(\epsilon_{HOMO} - \epsilon_{LUMO}) - J_{HOMO,LUMO} + K_{HOMO,LUMO}$. Now, both of these are 50% the desired singlet and 50% the hitherto missing third component of the triplet, and it is necessary to take linear combinations of the two wavefunctions in order to obtain the pure spin states. This will not change the average energy. Since we know that the energy of the third pure triplet component will have to be $-(\epsilon_{HOMO} - \epsilon_{LUMO}) - J_{HOMO}$, it follows that the energy of the pure singlet state must be $-(\epsilon_{HOMO} - \epsilon_{LUMO}) - J_{HOMO,LUMO} + 2K_{HOMO,LUMO}$ in order for the average to be correct.

The same answers for triplet and singlet energies can be derived by reversing the order of the two steps involved, i.e. adding an electron to LUMO first and removing one from HOMO afterwards. Both possibilities are schematically represented in Fig. 1.

To summarize, in the simple SCF picture, the triplet HOMO→LUMO excitation energy is less than the first ionization potential minus the first electron affinity, by an amount equal to $J_{HOMO,LUMO}$ and the singlet HOMO→LUMO excitation energy is less than the first ionization potential minus the first electron affinity, by an amount equal to $J_{HOMO,LUMO} - 2K_{HOMO,LUMO}$. The singlet-triplet splitting thus equals $2K_{HOMO,LUMO}$.

Estimating the Coulomb and exchange integrals from experimental data. If validity of the simple SCF model is assumed, it is possible to derive numerical values for the $J_{HOMO,LUMO}$ and $K_{HOMO,LUMO}$ integrals from experimental data as shown in the last three columns of Table 1. We are now able to compare the situation in azulene (**1**), anthracene (**3**), and naphthalene (**4**). The Coulomb integrals $J_{HOMO,LUMO}$ in **1** and **4** (molecules of about the same size) are equal, while that in **3** is somewhat smaller. This reflects a general trend: J tends to decrease slowly with increasing size of the molecule. This is physically reason-

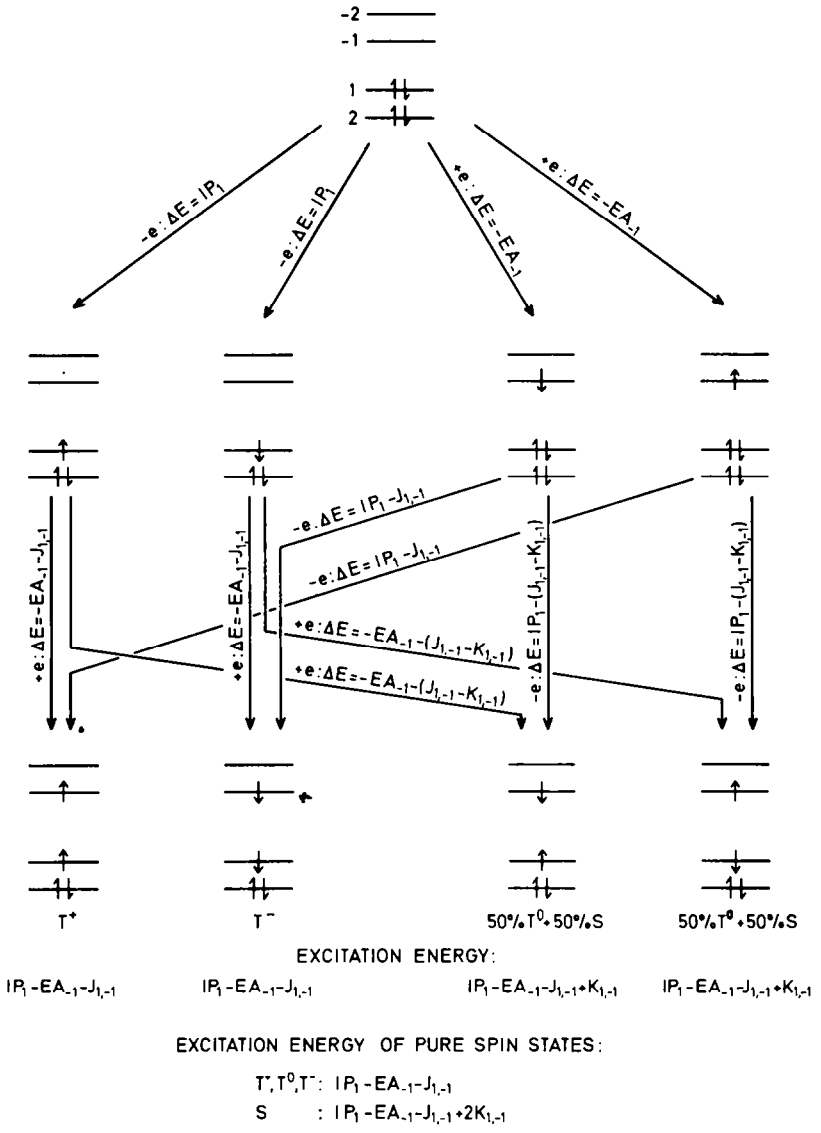


Fig. 1. Relation of excitation energies to orbital energies.

able considering that J describes the mutual interaction of two charge clouds extensively delocalized over the molecule.

The values of K are generally much smaller and they also tend to decrease slightly with increasing molecular size, so that the value of $-J+2K$ generally changes even less than J or 2K separately. However, comparison of $K_{HOMO,LUMO}$ for **1** and **4** shows that molecular size is not the only or even the most important factor in determining the value of K. We shall see later in more detail how this can be simply understood.

To summarize, the lower singlet (and triplet) HOMO→LUMO excitation energies of anthracene (**3**) compared with naphthalene (**4**) are due predominantly to changes in orbital energies (as reflected in the IP and EA values). The much lower singlet excitation energy of azulene (**1**) compared with naphthalene (**4**) is due about equally to changes in orbital energies between the two isomers (which can be understood simply[8] by reference to the common parent, [10]-annulene), and to a change in $2K_{HOMO,LUMO}$ (which can also be understood simply as shown below). The lower triplet excitation energy of azulene (**1**) compared with naphthalene (**4**) is due solely to changes in orbital energies. Comparison of azulene (**1**) with anthracene (**3**) is also instructive since their orbital energies are virtually identical: the relatively small difference in triplet excitation energies is due to J being smaller in the larger molecule; the much larger difference in singlet energies is mostly due to the large difference in 2K.

It is tempting to say that the main reason azulene is blue while anthracene is white, although they have similar ionization potentials and electron affinities, is that azulene has a much smaller singlet-triplet splitting. More correctly, the difference in the lowest singlet-singlet excitation energies, and thus in color and the small singlet-triplet separation can be both explained by the low value of $K_{HOMO,LUMO}$ for azulene (the spin-forbidden singlet-triplet absorption is extremely weak and does not affect color noticeably).

The next question, then, is, why is K so different in the two molecules?

The exchange integral: neutral alternant hydrocarbons

versus others. As pointed out above, the exchange integral $K_{HOMO,LUMO}$ is a measure of the repulsion of the overlap charge density $\psi_{HOMO}(1).\psi_{LUMO}(1)$ with identically distributed overlap charge density $\psi_{HOMO}(2).\psi_{LUMO}(2)$. If the two orbitals, HOMO and LUMO, are spread over different regions of space, their overlap density will be small and $K_{HOMO,LUMO}$ can hardly be large. In alternant hydrocarbons, each bonding orbital is paired with an antibonding orbital.[9] Putting an electron into one of them or the other leads to the same distribution of π-electron density over the atomic centers of the molecule, since the squares of the expansion coefficients of the MO's are equal (however, the contributions to the bond orders and thus to total bonding energy are exactly the opposite; after all, one of the orbitals is bonding, the other antibonding). The two orbitals thus occupy very much the same region in space, and their overlap density is relatively large. Since in neutral alternant hydrocarbons HOMO is paired with LUMO, one can see why $K_{HOMO,LUMO}$ is relatively large. Within this class of hydrocarbons, it slowly decreases with molecular size, similarly as does $J_{HOMO,LUMO}$. The similarity in the behavior of J and K is not surprising: because of the identical absolute values of expansion coefficients of HOMO and LUMO, the spatial distribution of the overlap density $\psi_{HOMO}(1).\psi_{LUMO}(1)$ is just like those of the (equal) charge densities $\psi_{HOMO}(1).\psi_{HOMO}(1)$ and $\psi_{LUMO}(2).\psi_{LUMO}(2)$. Of course, the repulsion of the overlap density with an identical one, $K_{HOMO,LUMO}$, is much smaller than that of the two just mentioned equal charge densities, since the overlap density is positive in some parts of space and negative in others. However, an increase in molecular size, and thus in the diffuseness of the charges, can clearly be expected to decrease the two repulsion energies, K and J, in a similar fashion.

In Fig. 2, this situation is contrasted with that found for molecules other than neutral alternant hydrocarbons. In these, orbital pairing need not, and usually does not, exist. As a result, HOMO and LUMO can frequently occupy quite different areas of space, and the overlap density as well as $K_{HOMO,LUMO}$ may be quite small. In Fig. 2, this is shown for azulene, but a similar situation occurs with many other non-alternant hydrocarbons, as well as charged alternant hydrocarbons (ions with an odd number of carbon atoms in conjugation, such as benzyl cation or anion).

The reason why azulene is blue while anthracene is white, in spite of their similar ionization potentials and electron affinities, thus ultimately can be sought in the fact that the HOMO and LUMO of azulene are localized largely in different parts of space in the azulene molecule, and this is only possible because azulene is non-alternant, while they are localized in the same parts of space in the anthracene molecule, as they must be, since anthracene is alternant.

Similarly, one can expect many other non-alternant hydrocarbons to have their HOMO→LUMO transition at longer wavelengths than would be expected on the basis of their ionization potentials and electron affinities. Inspection of the form of their HOMO and LUMO reveals how much they avoid each other in space and thus indicates how large the "anomaly" in the energy of their HOMO→LUMO transition will be.

Other experimental evidence. There is independent experimental evidence showing that in many non-alternant hydrocarbons, including azulene, HOMO is largely localized in different areas of space than LUMO, while in alternant hydrocarbons they are distributed very much in the same areas of space. For example, an inductive substituent can serve as a probe for change of electron density upon excitation at an atom to which it is attached. If the density increases upon excitation, an electron-donating substituent such as methyl will destabilize the excited state relative to the ground state and cause a blue shift of the transition. If the density decreases upon excitation, the same substituent will cause a red shift. This permits a rough mapping of the difference in the densities due to an electron in HOMO and in LUMO respectively. It turns out that the shifts are large for azulene,[10] and their signs and relative magnitudes agree with expectations based on Hückel MO's shown in Fig. 2. On the other hand, the shifts are small in alternant hydrocarbons.

An independent mapping of the spatial distributions of HOMO and LUMO is possible by analysis of the ESR spectra of the radical cation and radical anion of the hydrocarbons, respectively. Spin density distributions which can be derived from these measurements again show that HOMO and LUMO are distributed in like

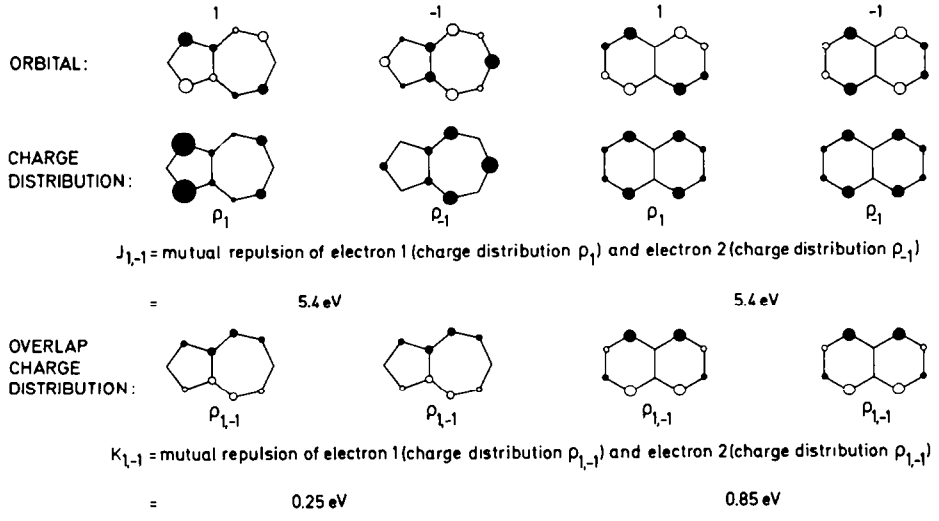


Fig. 2. Azulene and anthracene orbitals (1 = HOMO, −1 = LUMO). Charge distributions for determination of Coulomb integrals $J_{1,-1}$ and overlap charge distributions for determination of exchange integrals $K_{1,-1}$.

manner over the molecule of an alternant hydrocarbon, but can differ greatly in their spatial distribution in a molecule of a non-alternant hydrocarbon.[11]

It is interesting to note a relation between the "anomaly" shown by the HOMO→LUMO transitions of some non-alternant hydrocarbons and the weak intensity of such transitions, e.g. of the first transition in azulene. The intensity of the HOMO→LUMO transition is proportional to the square of the dipole moment of the overlap density $\psi_{HOMO}(1).\psi_{LUMO}(1)$. If HOMO and LUMO avoid each other in space, the overlap density is small, and as we have already seen, so is K, and the "anomaly" is large. If the overlap charge is very small in magnitude, it can hardly have a very large dipole moment, so one can expect that these transitions will in general also be fairly weak.

Correlations of singlet and triplet HOMO→LUMO *excitation energies with* HMO *energy differences.* The Hückel MO energies are in good linear relation to the SCF MO energies and also to experimental ionization potentials and electron affinities. Consequently, one can expect that Hückel HOMO–LUMO energy differences will correlate linearly with experimental HOMO→LUMO singlet excitation energies if $-J_{HOMO,LUMO} + 2K_{HOMO,LUMO}$ is a constant quantity or if it is linearly related to the HOMO–LUMO energy difference. We have already mentioned that $J_{HOMO,LUMO}$ is fairly constant, although it tends to decrease with increasing molecular size. Of course, the HOMO–LUMO energy difference generally also tends to decrease with increasing molecular size. Moreover, we have seen that for neutral alternant hydrocarbons $2K_{HOMO,LUMO}$ also changes very little and in such a way that $-J + 2K$ remains almost constant. It is therefore not surprising that a good linear correlation between Hückel HOMO–LUMO energy differences and HOMO→LUMO singlet excitation energies exists for these hydrocarbons.[1-3] As seen in the example of azulene, for other hydrocarbons 2K can be quite different. This then destroys the constancy of the term $-J + 2K$ and throws the point off the straight line in the plot.

It is now also understandable why almost all deviations from the regression line for benzenoid hydrocarbons occur in one sense: the theoretical transition energies are too high.[2,4,12] The only exception is linear polyenes and similar species with strong bond length alternation. This is not taken into account in the ordinary HMO model and leads to prediction of unrealistically low excitation energies. It is relatively simple to correct for this deficiency by allowing the resonance integral β to vary as a function of bond length, which in turn can be quite accurately guessed from the calculated bond order. This simple self-consistent version of HMO will, of course, still fail to rationalize the difference between anthracene and azulene.

Now, if the troublemaker in the Hückel correlation is K rather than J, one should expect a fair linear correlation for the triplet HOMO→LUMO excitation energies, for which only J enters. Indeed, it has been known for some time that such a correlation exists for the 0–0 bands of the lowest triplets and shows only one linear regression line for various kinds of hydrocarbons, including non-alternants.[13] Azulene still deviates somewhat, and, surprisingly, points for polyenes now also lie on the same regression line even though the resonance integral β is not varied with bond length. This might be caused by the use of 0–0 bands in the correlation rather than vertical transitions, for which the calculations are made (assuming identical geometries in ground and excited states).

Since J, but not 2K, appears to be fairly constant for a variety of molecules, it would seem best to view the Hückel HOMO–LUMO energy differences as approximating the triplet excitation energies (but for an additive constant), rather than averages of singlet and triplet excitation energies as is more commonly assumed.

Beyond the simple SCF model. The explicit use of electron repulsion terms has allowed us to obtain deeper insight into the nature of electronic excitation in π-electron molecules. The level at which discussion has been led is, however, still very far from rigorous. First of all, it was based on a semiempirical model limited to π electrons and using a very limited basis set of atomic orbitals. Second, even within the framework of this simplified semiempirical model, we did not deal with exact solutions of the Schrödinger equation, but only quite approximate ones. In order to proceed from the SCF level, at which our analysis was performed, to the exact solutions of the semiempirical model, one needs to introduce configuration interaction (CI). It then becomes harder to visualize the results in simple pictorial terms. Fortunately, for the kind of molecules with which we have been dealing, even the most extensive CI calculations agree that for the ground state and the HOMO→LUMO excited state the mixing of configurations represents only second-order corrections, so that already the simple SCF level should be meaningful. However, a reader who is more deeply interested in the problems of electronic excitation and wants to find out about interpretation of other transitions in the spectra of π-electron systems (and of other molecules) is referred to literature describing the configuration interaction method.[14].

REFERENCES

[1]A. Streitwieser, *Molecular Orbital Theory for Organic Chemists*, p. 220. Wiley, New York (1961). (The assignment of the azulene HOMO→LUMO excitation used in this book is incorrect.)

[2]J. Koutecký, J. Paldus and R. Zahradník, *J. Chem. Phys.* **36**, 3129 (1962); R. Zahradník, *Fortschr. Chem. Forsch.* **10**, 1 (1968).

[3]E. Heilbronner and J. N. Murrell, *J. Chem. Soc.* 2611 (1962).

[4]J. Koutecký, P. Hochman and J. Michl, *J. Chem. Phys.* **40**, 2439 (1964).

[5]For a more detailed discussion, see M. J. S. Dewar, *The Molecular Orbital Theory of Organic Chemistry*, p. 62. McGraw-Hill, New York (1969).

[6]J. Killingbeck, *Mol. Phys.* **25**, 455 (1973); J. P. Colpa and R. E. Brown, *Ibid.* **26**, 1453 (1973).

[7]T. Koopmans, *Physica* **1**, 104 (1933).

[8]E. Heilbronner, *Non-benzenoid Aromatic Compounds* (Edited by D. Ginsburg), p. 185. Interscience, New York (1959).

[9]C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Phil. Soc.* **36**, 193 (1940).

[10]C. A. Coulson, *Proc. Phys. Soc.* **A65**, 933 (1952); H. C. Longuet-Higgins and R. G. Sowden, *J. Chem. Soc.* 1404 (1952).

[11]F. Gerson and J. H. Hammons, *Nonbenzenoid Aromatics* (Edited by J. P. Snyder), Vol. 2, p. 81. Academic Press, New York (1971).

[12]R. Zahradník, C. Párkányi, J. Michl and V. Horák, *Tetrahedron* **22**, 1341 (1966).

[13]R. Zahradník, I. Tesařová and J. Pancíř, *Coll. Czech. Chem. Commun.* **36**, 2867 (1971).

[14]L. Salem, *The Molecular Orbital Theory of Conjugated Systems*, p. 408. Benjamin, New York (1966); F. L. Pilar, *Elementary Quantum Chemistry*, Chap. 19. McGraw-Hill, New York (1968); N. Mataga and T. Kubota, *Molecular Interactions and Electronic Spectra*, p. 64. Marcel Dekker, New York (1970).