Spectroscopic and Photochemical Investigation of the Triplet States of *p*-Diiodobenzene and Other Iodoaromatics

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Abstract: The lowest triplet state of *p*-diiodobenzene is shown to be dissociative in experiments where the triplet state is generated directly by optical excitation in the first $S_0 \rightarrow T$ absorption band (3660 A). In methylcyclohexane solutions the quantum yield for production of I_2 is 0.26 ± 0.02 both at 3660 and 2537 A. Studies of the phosphorescence excitation (PE) spectra of naphthalene-doped crystals of *p*-diiodobenzene and of other iodobenzene derivatives indicate that intermolecular transfer of triplet-state excitation energy is very inefficient. This inefficiency in energy transfer is attributed to dissociation of the triplet-state molecules at a rate which is much faster (factor of 10^3) than nearest neighbor triplet–triplet energy transfer. A triplet-state lifetime on the order of 10^{-13} sec is indicated for *p*-diiodobenzene. In contrast to the behavior of *p*-diiodobenzene, iodobenzene, and *p*-iodotoluene, other iodoaromatics (2-iodobiphenyl, 2-iodonaphthalene) with lower energy triplet states exhibited normal behavior when studied by PE techniques.

Recently Castro and Hochstrasser published the single-crystal $S_0 \rightarrow T$ absorption spectra of various halogenated benzene derivatives, and a comparison of the spectra of the *para*-disubstituted compounds provides some rather interesting contrasts.[3,4]

The bands in the *p*-diiodobenzene $S_0 \rightarrow T$ absorption spectrum were quite broad (~200-cm^{-1} half-widths) and exhibited significant Davydov splittings (~120 cm^{-1}), and the structured $S_0 \rightarrow T$ absorption (origin at 3650 A) was superimposed on an unassigned broad continuum absorption which extended to even longer wavelengths (~3800 A). In contrast to this, the $S_0 \rightarrow T$ absorption spectra of *p*-dichloro- and *p*-dibromobenzene consisted of many sharp lines (half-widths less than 1 cm^{-1}) which exhibited little or no Davydov splitting. Although certain of these differences in spectral behavior are undoubtedly due to the fact that the crystal structures of *p*-dichloro- and *p*-dibromobenzene are different from that of *p*-diiodobenzene, other effects may well be operative.

On the basis of a preliminary investigation of the $S_0 \rightarrow T$ absorption spectrum of *p*-diiodobenzene crystals by phosphorescence excitation techniques, we suggested that some of the features observed in the direct $S_0 \rightarrow T$ absorption spectrum might be due to predissociation.[5] In the present study we have extended these spectroscopic observations to other iodoaromatics and have investigated the photochemistry of *p*-diiodobenzene in its triplet state. These new results confirm our earlier suggestion that the lowest triplet state of *p*-diiodobenzene is dissociative and provide a possible explanation of certain of the unusual features in the $S_0 \rightarrow T$ absorption spectrum of this compound.

Experimental Section

1. Methods. The investigation of $S_0 \rightarrow T$ absorption spectra by the phosphorescence excitation (PE) method has been described in detail elsewhere.[5,6] In the present study each host crystal was doped with a small amount of a guest impurity which had a lower energy triplet state than that of the host. The guest molecules functioned as traps of triplet-state energy in the crystal, and phosphorescence excitation spectra were then obtained by monitoring the variation in the intensity of the *guest phosphorescence* (I_p) with the wavelength of excitation (λ_{ex}). The relevant energy levels for the systems which we studied are illustrated in Figure 1.

All phosphorescence excitation (PE) spectra were obtained on crystalline samples at 77°K using a conventional phosphoroscope.[5,6] Direct $S_0 \rightarrow T$ absorption spectra were obtained with a Cary Model 14 spectrophotometer. An Osram 200-w superpressure mercury lamp was used in conjunction with a Bausch and Lomb compact grating monochromator as the light source in the photochemical studies. Absolute photon intensities were measured with a calibrated Eppley thermopile (sensitivity = 0.196 μv/μw).

2. Materials. *p*-Diiodobenzene, *p*-iodotoluene, 2-iodobiphenyl, 2-iodonaphthalene, and chrysene were purified by recrystallization. Naphthalene and phenanthrene were purified by zone refining. Reagent grade iodobenzene was used without further purification. 2-Methyltetrahydrofuran was distilled from sodium ketyl through a 4-ft column packed with glass helices. Doped crystals were prepared from the melt.

Results

1. Direct Singlet–Triplet Absorption Spectra. The $S_0 \rightarrow T$ absorption spectrum of *p*-diiodobenzene was measured both at room temperature and at 77°K in 2-methyltetrahydrofuran. The low-temperature spectrum is presented in Figure 2a. At 77°K the extinction coefficient of the first $S_0 \rightarrow T$ absorption band (3650 A) was found to be 0.8, in reasonable agreement with the value of 1.0 reported by Castro and Hochstrasser.[3] At room temperature the apparent extinction coefficient of the 3650-A band increased to about 1.0 due to a small contribution (10–20%) from the tail of the $S_0 \rightarrow S$ absorption band. This observation is particularly significant in terms of the interpretation of the photochemical studies, since it demonstrates that at room temperature 80–90% of the light absorption at 3650 A is due to a $S_0 \rightarrow T$ transition.

2. Phosphorescence Excitation Spectra. The PE spectra of crystalline samples of the iodoaromatics containing naphthalene, phenanthrene, or chrysene as guests were investigated at 77°K, and these results were presented in Figure 2c–e. In each case the solubility of the guest molecules in the host matrix was established

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[1] NASA Predoctoral Fellow.

[2] Alfred P. Sloan Fellow.

[3] G. Castro and R. M. Hochstrasser, *Mol. Crystals*, **1**, 139 (1966).

[4] G. Castro and R. M. Hochstrasser, *J. Chem. Phys.*, **44**, 412 (1966).

[5] A. Marchetti and D. R. Kearns, *J. Am. Chem. Soc.*, **89**, 768 (1967).

[6] W. Rothman, A. Case, and D. R. Kearns, *J. Chem. Phys.*, **43**, 1067 (1965); D. R. Kearns and A. Case, *J. Am. Chem. Soc.*, **88**, 5087 (1966); R. Borkman and D. R. Kearns, *Chem. Commun.*, **14**, 446 (1966).

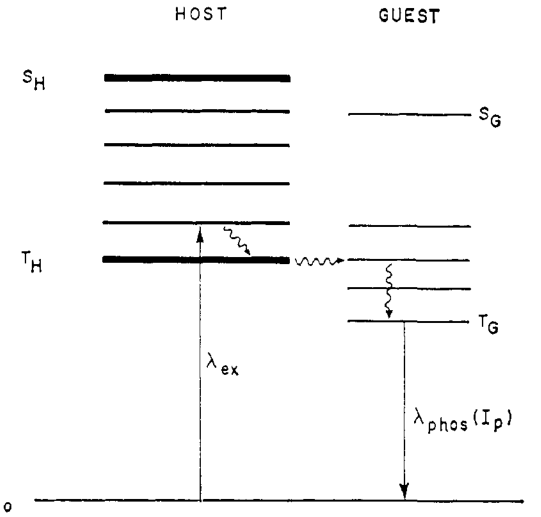

Figure 1. Schematic energy-level diagram indicating the relative energies of the excited singlet and triplet states of the host and guest molecules. Solid lines indicate radiative transitions and wavy lines indicate radiationless transitions.

by the fact that strong phosphorescence characteristic of the guest molecule was observed when the crystal was excited in the $S_0 \rightarrow S$ absorption band of the guest, and by the fact that there was a significant heavy-atom effect on the triplet-state lifetime of the guest. The triplet-state lifetime of naphthalene in *p*-diiodobenzene, for example, was 15 msec.[7] In the case of the iodobenzene derivatives where naphthalene was the guest, the external heavy-atom effect was sufficiently pronounced that even the $S_0 \rightarrow T$ absorption spectrum of the naphthalene guest molecules could easily be observed (see Figure 2c–e). In view of this, it was surprising that there was little or no evidence in the PE spectra of the three iodobenzene derivatives (with perhaps the exception of *p*-iodotoluene) for the relatively strong host $S_0 \rightarrow T$ absorption bands which are known to occur in the 3700–3000-A region.[3,8] In contrast to the very anomalous behavior of the iodobenzene derivatives, the $S_0 \rightarrow T$ absorption spectra of crystalline samples of many other halogenated benzenes and iodoaromatics with lower energy triplet states have easily been obtained by the PE method (see Figure 3).[5,6]

3. Photolysis of *p*-Diiodobenzene. Previous photochemical studies have established that most iodobenzene derivatives are unstable toward ultraviolet excitation, with quantum yields for photodissociation into phenyl radicals and iodine atoms usually approaching unity.[9–11] Although it is not yet known whether the dissociation occurs from an excited singlet or triplet state, our preliminary investigation of the PE spectrum of *p*-diiodobenzene suggested that the triplet state is dissociative.[5] To test this suggestion we investigated the reactivity of triplet state *p*-diiodobenzene molecules generated directly by excitation in the 3650-A $S_0 \rightarrow T$ absorption band.

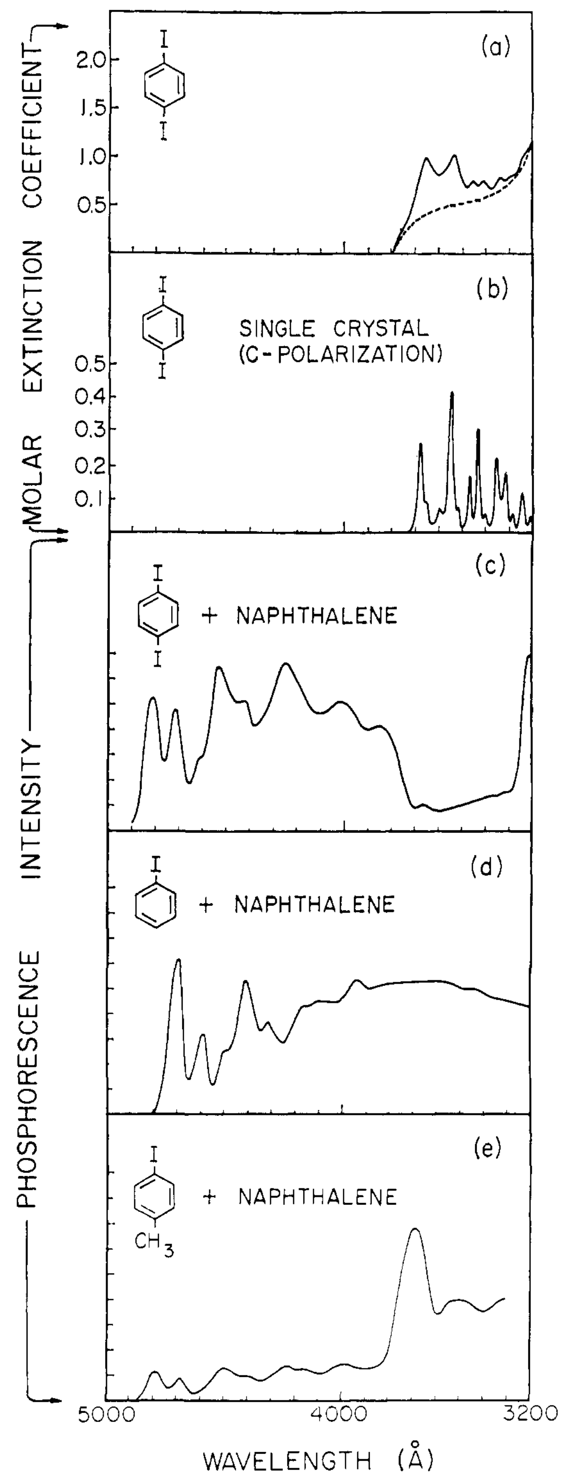

Figure 2. Singlet-triplet absorption spectra of various iodoaromatic compounds: (a) direct $S_0 \rightarrow T$ absorption spectrum of *p*-diiodobenzene, taken from ref 3 (the unassigned continuum absorption is indicated by the dashed curve); (b) direct $S_0 \rightarrow T$ absorption spectrum of a single crystal of *p*-diiodobenzene, taken from ref 3; (c) PE spectrum of *p*-diiodobenzene doped with naphthalene; (d) PE spectrum of iodobenzene doped with naphthalene; (e) PE spectrum of *p*-iodotoluene doped with naphthalene.

In separate experiments 1-cm thick quartz cells containing nondegassed 0.1 *M* solutions of *p*-diiodobenzene in cyclohexane were irradiated at 3660 and 2537 A. Under the conditions of illumination, the initially colorless solutions rapidly (several minutes) developed a purple color characteristic of molecular iodine. From

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(7) G. G. Giachino and D. R. Kearns, unpublished results.

(8) D. S. McClure, N. W. Blake, and P. L. Hanst, *J. Chem. Phys.*, 22, 255 (1954).

(9) W. Wolf and N. Kharasch, *J. Org. Chem.*, 26, 283 (1961).

(10) N. Kharasch, W. Wolf, T. J. Erpelding, P. G. Naylor, and L. Tokes, *Chem. Ind.* (London), 1720 (1962).

(11) J. A. Kampmeier and E. Hoffmeister, *J. Am. Chem. Soc.*, **84**, 3787 (1962).

a measurement of the I_2 absorption and of the total number of photons absorbed, the quantum yield, Φ_{I_2}, for the formation of molecular iodine was calculated.[12] The results were $\Phi_{I_2}(2537\ A) = 0.24$ and $\Phi_{I_2}(3660\ A) = 0.28$, with an uncertainty of ± 0.02.

No evidence for the formation of I_2 was observed with the crystalline samples, but this can probably be attributed to a cage effect. There was significant production of I_2 when molten samples were irradiated.

Discussion

The experiments involving direct optical excitation of *p*-diiodobenzene to its lowest triplet state demonstrate that the triplet state of this compound is unstable with respect to dissociation into products which ultimately form I_2. Although $\Phi_{I_2}(3660\ A)$ was only 0.28, the quantum yield for the initial photodissociation process must be on the order of unity for the following reasons. In the absence of a chain reaction Φ_{I_2} could at most be 0.5. Taking this value, together with Lampe and Noyes's factor of 0.6 to account for cage recombination,[13] we could expect Φ_{I_2} to at most be on the order of 0.30, in agreement with the experimentally observed value of $\Phi_{I_2} = 0.28 \pm 0.02$. These observations on the photochemistry of *p*-diiodobenzene provide a very plausible explanation for the apparent lack of triplet-state energy transfer in the iodobenzene crystals.

The phosphorescence excitation spectra of crystalline samples of three iodobenzene derivatives were measured at 77°K and all behaved anomalously. In each case there was little or no evidence for the strong host $S_0 \rightarrow T$ absorption, in spite of the fact that the weak $S_0 \rightarrow T$ absorption of the naphthalene guest molecules was easily observed. If transfer of triplet-state energy from the iodobenzenes to naphthalene were efficient, then absorption of light by the host molecules should have been much more effective in populating the naphthalene triplet states than direct excitation in the weak $S_0 \rightarrow T$ absorption band of the naphthalene guests. The behavior of the iodobenzenes is to be contrasted with normal behavior of naphthalene-doped *p*-dibromobenzene crystals (shown in Figure 3a). In this case excitation in host $S_0 \rightarrow T$ absorption bands was 10^3 times more effective in generating naphthalene triplets than was excitation in the naphthalene $S_0 \rightarrow T$ absorption bands. The fact that 2-iodonaphthalene and many other halogenated benzene derivatives (see Figure 3) also exhibited normal crystal PE spectra[5] only emphasizes the peculiar behavior of the iodobenzenes.

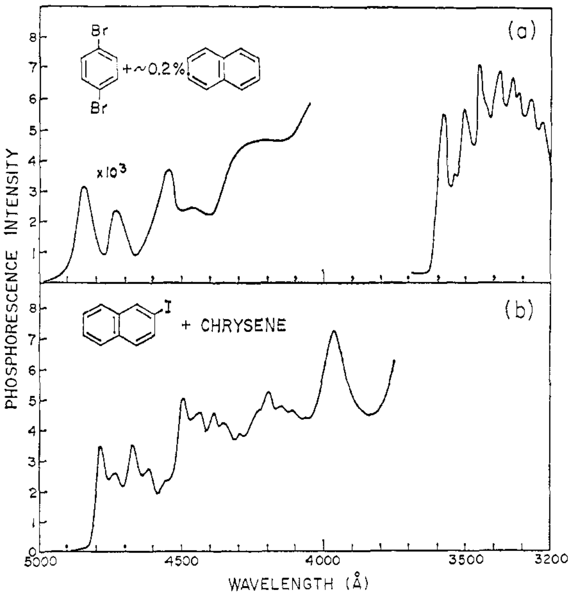

Figure 3. Phosphorescence excitation spectra of some haloaromatics: (a) PE spectrum of naphthalene-doped *p*-dibromobenzene illustrating the significant ($\sim 10^3$) increase in the naphthalene phosphorescence produced by exciting in the host $S_0 \rightarrow T$ absorption band; (b) PE spectrum of 2-iodonaphthalene doped with chrysene showing the strong host $S_0 \rightarrow T$ absorption bands. Because of poor sensitivity, it was not possible to detect the much weaker $S_0 \rightarrow T$ absorption bands of the chrysene guest molecules.

The $S_0 \rightarrow T$ absorption of the naphthalene guests provides a convenient internal standard for calibrating the PE measurements. The extinction coefficient for the perturbed $S_0 \rightarrow T$ absorption band of naphthalene in *p*-diiodobenzene is probably about 5×10^{-3},[14] whereas the molar extinction coefficient for the $S_0 \rightarrow T$ transition of *p*-diiodobenzene is about 0.8.[3] Therefore, if we conservatively assume that only those triplet-state *p*-diiodobenzene molecules which have naphthalene molecules as neighbors are capable of sensitizing the triplet state of a naphthalene molecule, we predict that excitation in the host $S_0 \rightarrow T$ absorption band should be on the order of $6 \times 0.8/(5 \times 10^{-3}) \simeq 10^3$ times more effective in generating naphthalene triplet states than excitation in the naphthalene $S_0 \rightarrow T$ band.[14,15] Experimentally, we observed a decrease (factor of 2–4) in the PE spectrum when the doped crystals were excited in the host $S_0 \rightarrow T$ absorption band. This observation was not an artifact produced by too large optical density, since the same results were obtained with thick and thin (0.5 mm) crystals. We must conclude from these observations that the triplet-state energy of *p*-diiodobenzene molecules is dissipated at a rate which is $2\text{–}4 \times 10^3$ times faster than the rate at which triplet energy is transferred to a naphthalene neighbor. In view of the dissociative character of the triplet state of *p*-diiodobenzene in solution, it seems reasonable to conclude that dissociation is also the process which competes with the transfer of triplet-state energy from *p*-diiodobenzene to naphthalene.[16]

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[12] The photon intensity at 3660 A was 1.5×10^{16} photons/sec, and 3×10^{15} photons/sec at 2537 A. Irradiation experiments were carried out using 0.1 *M* solutions of *p*-diiodobenzene in methylcyclohexane. At 2537 A all of the incident photons were absorbed, whereas at 3660 A direct absorption measurements indicated that only 21% of the light was absorbed. After 30 min irradiation at 3660 A the optical density at 5300 A due to I_2 was 0.25 (1-cm cell with 3.7-ml volume), whereas 30 min of irradiation at 2536 A produced an OD of 0.27 at 5300 A (1-cm cell with 3.1-ml volume). From these data we calculate $\phi_{I_2}(3660\ A) = 0.28$; $\phi_{I_2}(2537\ A) = 0.24$.

[13] F. W. Lampe and R. M. Noyes, *J. Am. Chem. Soc.*, **76**, 2140 (1954).

[14] S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964).

[15] Each naphthalene was assumed to have six *p*-diiodobenzenes as near neighbors.

[16] A referee has suggested that triplet excimer formation might be the process competing with energy transfer to naphthalene. Although we cannot definitely rule out this alternative explanation, it seems unlikely for several reasons. G. Castro and R. M. Hochstrasser [*J. Chem. Phys.*, **45**, 4352 (1966)] have shown that both chloro- and bromobenzene derivatives exhibit triplet excimer formation, and yet all of these systems behaved normally when studied by excitation techniques.[5] In order for excimer formation to quench energy transfer, the triplet state of the excimer would have to lie lower in energy than that of the guest. In the naphthalene-doped systems this would require a shift of over 6000 cm^{-1} *in the 0–0 band of the triplet excimer* emission relative to the 0–0 band in absorption, and this does not seem reasonable. Finally, one might expect that molecules which have lower lying triplet states (iodobiphenyl and iodonaphthalene) would also show excimer trapping of triplet energy, but they do not.

An estimate of the rate constant for this dissociation process can be obtained in the following way. Under favorable conditions triplet–triplet energy transfer in solution is found to be diffusion controlled, indicating that the nearest neighbor triplet–triplet energy-transfer rate constant is probably on the order of 10^9–10^{10}/sec.[17] If we assume a similar nearest neighbor energy-transfer rate constant for the crystalline systems which we studied, then the rate constant for the dissociation of *p*-diiodobenzene triplet states must be $\simeq(4 \times 10^3) \times (10^9\text{–}10^{10})/\text{sec} = 4 \times 10^{12}$ to 4×10^{13}/sec. The lifetime of the lowest triplet state of *p*-diiodobenzene must correspondingly be 2.5×10^{-13} to 2.5×10^{-14} sec.

It was noted that a significant portion of the $S_0 \rightarrow T$ absorption of *p*-diiodobenzene is due to a broad unassigned continuum which extends to *longer wavelengths than the structured* absorption.[3] This continuum absorption presumably is not due to impurities since it also appears in highly purified samples. Apparently it corresponds to a $S_0 \rightarrow T$ transition which is different in character from the one which gives rise to the structured absorption. Since the $n \rightarrow \sigma^*$ transitions in the alkyl iodides have significant intensities as far out as 3500 A,[14,18] we suggest that the long-wavelength continuum absorption in *p*-diiodobenzene also be assigned as an $n \rightarrow \sigma^*$ transition. Such an assignment would also account for the diffuseness of the absorption and the dissociative character of the triplet state. Alternatively, and less likely, it is possible that the continuum absorption represents a transition to a second π,π triplet state which, in order to account for lack of structure, we must presume dissociates with a rate constant which is even larger than 4×10^{13}/sec.

As a result of our assignment of the continuum absorption, we are inclined to attribute the broadness in structured $S \rightarrow T_{\pi,\pi}$ absorption to mixing between the discrete vibronic levels of the $T_{\pi,\pi}$ state and the underlying continuum T_{n,σ^*} levels.

The high-resolution crystal absorption spectra of other iodobenzene derivatives have not yet been reported, but, in view of the unusual PE spectra which these compounds also exhibited, anomalies similar to those observed in the $S_0 \rightarrow T$ absorption spectrum of *p*-diiodobenzene may be anticipated.

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(18) K. Kimura and S. Nagakura, *Spectrochim. Acta*, 17, 166 (1961)

Alternating Molecular Orbital Delocalization Energies of Symmetrical Alternant Polycyclic Polyenes.

$4n + 2$, $6n + 2$, $8n - 2$, $8n + 2$, and $8n + 4$ Effects

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Abstract: For a systematic series of symmetrical alternant polycyclic polyenes, LCAO–MO resonance energies calculated at any level of elaboration are divided into two parts: the first a reference function, the second the original simple Hückel delocalization energy multiplied by a constant amplifying factor. The factor can be chosen to minimize and render unimportant the oscillatory component of the reference function. It follows that alternations at any level of elaboration can be at least adequately studied by means of SHMO theory. Three $8n$ effects and a triple $2 + 6n$ effect in selected series are described and shown to involve the same algebraic features as the $2 + 4n$ effect of the annulenes.

Effective elaboration of the simple Hückel molecular orbital (SHMO) method of calculating resonance energies of aromatic hydrocarbons is limited by restrictions imposed by the assumed LCAO wave function. One of the restrictive effects appears in the alternating calculated stabilizations of the annulenes and of systematic series of symmetrical alternant polycycles.

It is shown that quantitatively, for the annulenes, elaboration merely multiplies the amplitudes of the $2 + 4n$ alternation by a constant factor as large as 3.4. For other series, there must be for each structure a single average exchange constant that will lead to the correct delocalization energy. Since this average β_N cannot vary much more through the series than the β_N of the annulenes, the conclusion for the annulenes must be applicable with adequate accuracy to alternating effects in other symmetrical series.

With the aid of a factoring method described in a separate section, the alternations in four symmetrical series are shown to be essentially the original $2 + 4n$ effect appearing with different periodicities. This means that the dubiously low result for cyclobutadiene is carried into the calculations for the depressed members of all the series. For this reason, the general reliability of any LCAO method, regardless of corrective elaboration, becomes questionable.