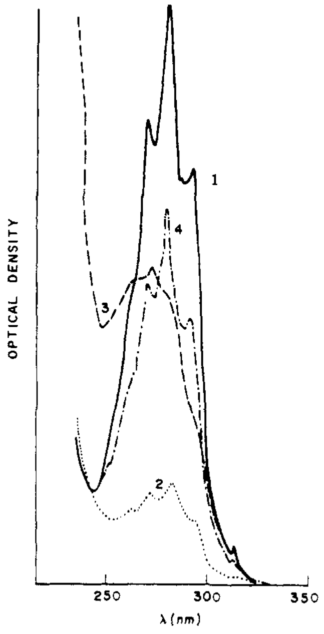


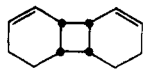
Figure 1. Absorption spectrum of 10^{-3} M Iα in methylcyclohexane (degassed), curve 1; after irradiation at 300 nm, curve 2; after heating to *ca.* 75°, curve 3; after irradiation at 254 nm, curve 4. The operations were sequential.

nm, higher ϵ). Both II and III are converted substantially to Iα upon irradiation with 254-nm light.

A colorless crystalline product consisting of nearly pure II crystallizes upon irradiation of an almost saturated degassed solution (at *ca.* 15°) of Iα in methylcyclohexane. Since II is thermally labile it is impossible to obtain it completely free from III. The uv spectrum of II exhibits a broad plateau (285–265 nm, $\epsilon \leq 2000$), reminiscent of dianthracene[7] and consistent with the assigned structure. We have assigned the *syn* structure to II because it appears to be formed from the excimer which undoubtedly has the configuration of greatest overlap. The uv spectrum of the *anti* isomer would probably resemble that of *o*-xylene more closely than does the spectrum of II.

The nmr spectrum of II ($CDCl_3$, 10°) is also in accord with this structure: τ 7.3–8.3 (m, 3.3, propyl chain); 6.3 (m, 1, methine); 3.9, 3.65, 3.1–3.5 (unsym d, m, $J = 6$, vinyl, vinyl, aromatic). It is not possible to obtain meaningful ratios of vinyl to vinyl or to aromatic protons because the chemical shifts are so similar. This similarity of the vinyl protons is expected for structure II. Decoupling the methine proton yields an AB quartet for the vinyl protons with the two halves centered at τ 3.55 and 3.90. The absorption (τ 3.55) coupled to the methine proton together with its absorption at τ 6.3 are similar to those (τ 3.52 and 6.09) reported for the corresponding protons in benzobicyclo[2.2.2]octadiene.[8]

The cyclobutane isomer III is obtained by boiling the crude photoproduct from Iα in $CHCl_3$ followed by crystallization from $CHCl_3$–hexane (mp 179–181° dec).[9] Its spectra indicate that it is the Cope rearrangement product of II. The uv spectrum of III has a broad band at 265 nm (ϵ 1.02 × 10^3), which is similar to that of 1,2-dihydronaphthalene (259 nm, ϵ 9.55 × 10^3).[10] The hypochromism is attributed to interaction between the two chromophores.[11] The nmr spectrum ($CDCl_3$) of III exhibits peaks at τ 7.5–8.2 (m, 3, propyl chain), 6.7 (m, 1, methine), 4.45 (unsym d of m, 1, nonbenzylic vinyl), 3.8 (unsym d, 1, benzylic vinyl), 3.1–3.5 (m, 4, aryl), and is in accord with that expected for structure III. Both the methine and vinyl protons of III absorb upfield from those of II. The chemical shifts for these protons in the model system IV (τ 7.12 and 4.25, respectively) are similarly shifted upfield from those in benzobicyclo[2.2.2]octadiene.[12] Cyclobutane III reverts slowly to Iα upon melting, but is stable in solution at 100° for at least 1 hr.



IV

Consideration of the steric strain in the corresponding hypothetical photoisomers of Iβ suggests that 1, 1′, 2, 2′ (2 + 2) addition should be as available to the intramolecular excimer from Iβ as to that from Iα. Since Iβ shows no tendency to photoisomerize, the (2 + 2) cycloaddition product, III, probably does not result directly from the Iα excimer, even though some of it is always found in the initial photolysate.

Species such as 1,2-di-α-naphthylethane and 1,4-di-α-naphthylbutane, which do not exhibit excimer fluorescence at 25°, do not photodimerize. We also found no evidence of photodimerization upon irradiation of pure liquid α-methylnaphthalene. The stabilization of the intramolecular excimer provided by the propane chain, attributable to a decrease in the entropy of association, appears to be responsible for these differences in behavior. The dimerization reaction obviously has an activation energy, and the normal naphthalene intermolecular excimer is too short-lived at room temperature for bond formation to occur. Self-quenching of naphthalene also decreases as the temperature increases.[13] The thermal instability of the excimer is a reflection of the increasing free energy of the excimer with temperature, due to the $T\Delta S$ term. We also photolyzed 1,3-diphenylpropane but found no sign of photodimerization; however, some fulvene derivative apparently was formed.

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[7] K. S. Wei and R. Livingston, *Photochem. Photobiol.*, **6**, 229 (1967).

[8] K. Tori, Y. Takano, and K. Kitahonoki, *Chem. Ber.*, **97**, 2798 (1964).

[9] *Anal.* Calcd for $C_{23}H_{20}$: C, 93.20; H, 6.80; mol wt, 296. Found: C, 93.48; H, 6.94, mol wt, 296 (osmometric in CCl_4).

[10] W. Hückel, E. Vevera, and U. Worffel, *Chem. Ber.*, **90**, 901 (1957).

[11] J. N. Murell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, New York, N. Y., 1963, Chapter 7.

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[13] B. Stevens and J. T. Dubois, *Trans. Faraday Soc.*, **62**, 1525 (1966).

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Excimer Fluorescence and Dimer Phosphorescence from a Naphthalene Sandwich Pair

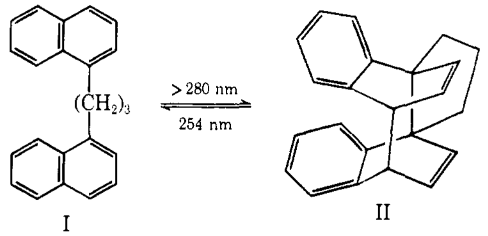
Sir:

The question of the possible existence of triplet excimers, analogous to the well-known singlet excimers, has been of interest during the last few years. There are few experimental results available because of the difficulty of measuring phosphorescence from fluid media and the difficulty of obtaining molecular pairs of suitable geometry in rigid matrices.

In this note we report studies of the luminescence of a species which is essentially a sandwich pair of naphthalene molecules in a rigid matrix at 77°K. The fluorescence of the pair is typical of a naphthalene excimer, but the phosphorescence is not very different from that of the monomer, indicating that the interaction in the triplet state of a sandwich pair is much less than in the excited singlet state.

Lim and Chakrabarti[1] reported an unusually broad, red shifted phosphorescence from concentrated solutions of chlorobenzene in EPA at 77°K. It was interpreted as excimer phosphorescence, presumably from sandwich pairs trapped in the matrix, although no mention of excimer fluorescence was made. These authors also questioned the assignment[2] of the anomalous luminescence of crystalline dibromobenzene. Recently the delayed luminescence spectra of solutions of naphthalene or phenanthrene at low temperatures have been interpreted as involving excimer phosphorescence.[3] On the other hand Kearns and Chambers[4] reported that dye molecule pairs in rigid glasses show very little change in their phosphorescence from that of the monomer.

During a study of intramolecular excimer formation and fluorescence quenching in various dinaphthylalkanes we found[5] that 1,3-bis(1-naphthyl)propane (I) photodimerized (λ >280 nm) to the anthracene-like dimer II. Further, upon irradiation with a low-pressure Hg lamp, solutions of II (77 or 300°K) regenerate I, identified by its characteristic ultraviolet spectrum.



The photolytic cleavage of II in methylcyclohexane at 77°K generates I, having a sandwich configuration of the two naphthalene nuclei,[6] an unstable geometry. The luminescence spectra (λ_{exc} 313 nm) of the sandwich pair are shown in Figure 1a. After thawing and refreezing the sample, the spectra in Figure 1b are obtained. The ultraviolet absorption spectrum of the photolyzed sample is consistent with a sandwich pair configuration; after thawing and refreezing it reverts to that of I.

The initial fluorescence of the photodissociated sample is similar to the excimer fluorescence of various naphthalenes in fluid solution,[7–9] including the intramolecular excimer formed by both I and the isomeric 2-naphthyl compound.[10] The final fluorescence spectrum is identical with that of I at low temperatures, essentially that of 1-methylnaphthalene.

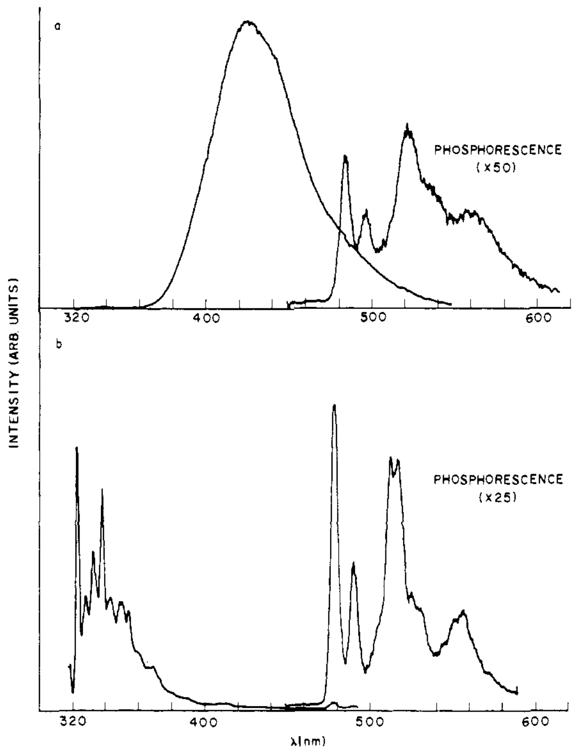


Figure 1. (a) Luminescence spectra (excited at 313 nm) of the sandwich naphthalene pair obtained from II by photolysis with 254-nm light in methylcyclohexane at 77°K. (b) Luminescence spectra of the above sample after melting and refreezing. The intensity scale is not corrected for spectrometer response but is the same for both sets of spectra.

The final phosphorescence spectrum is typical of a simple naphthalene and is identical with that of I. We assign the initial phosphorescence spectrum to the sandwich pair and conclude that a triplet excimer is not formed. The interaction between the naphthalene nuclei is much weaker than in the singlet excimer case. The first band of the dimer phosphorescence spectrum is shifted 250 cm^{-1} to the red of the monomer, and the vibrational structure is altered with more of the intensity in the lower energy part of the spectrum. The center of gravity of the dimer spectrum (after correction for spectrometer response which changes rapidly above 500 nm, an EMI 6256S photomultiplier was used) is shifted about 10^3 cm^{-1} to lower energy. The corresponding shift for singlet excimers is about 6×10^3 cm^{-1}. We found the lifetime of the dimer phosphorescence to be 1.5 sec, while that of the monomer is 2.4 sec.

These results establish that triplet naphthalene does not form an excimer with a second, presumably suitably oriented (*cf.* the fluorescence) naphthalene molecule at 77°K. If the formation of an excimer were hindered because of an activation energy we can set a lower limit

(1) E. C. Lim and S. K. Chakrabarti, *Mol. Phys.*, 13, 293 (1965).

(2) G. Castro and R. M. Hochstrasser, *J. Chem. Phys.*, 45, 4352 (1966).

(3) J. Langelaar, R. P. H. Rettschnick, A. M. F. Lambooy, and G. J. Hoytink, *Chem. Phys. Lett.*, 1, 609 (1968).

(4) R. W. Chambers and D. R. Kearns, *J. Phys. Chem.*, 72, 4718 (1968).

(5) E. A. Chandross and C. J. Dempster, *J. Amer. Chem. Soc.*, 92, 703 (1970).

(6) For the analogous photolytic dissociation of dianthracene, see E. A. Chandross, *J. Chem. Phys.*, 43, 4175 (1965); E. A. Chandross, J. Ferguson, and E. G. McRae, *ibid.*, 45, 3546 (1966).

(7) E. Döller and Th. Förster, *Z. Phys. Chem.*, 31, 274 (1962).

(8) B. Stevens and M. I. Ban, *Trans. Faraday Soc.*, 60, 1515 (1964).

(9) B. K. Selinger, *Aust. J. Chem.*, 19, 825 (1966).

(10) C. J. Dempster and E. A. Chandross, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, PHYS 25.

of 4 kcal mole^{-1} for this E_a, based on a rate of less than 1 sec^{-1} and an A factor $\geq 10^{12}$. It does not seem reasonable that there should be such a barrier in view of the absence of a barrier to formation of a singlet excimer, which rules out any steric factors, either intramolecular or involving the matrix. We cannot rule out the possibility that the preferred geometry of a triplet excimer is not the same as the symmetrical sandwich preferred by the singlet isomer, and that this unknown configuration is not attainable in the rigid matrix. If such a barrier were to exist it would not interfere with excimer formation at the temperatures employed by Langelaar, *et al.*[3] We think it unlikely that such a barrier does really exist. Our results do not rule out the interpretation of Langelaar, *et al.* However, the equilibrium constant for formation of a triplet excimer would be small, probably less than 1, even at low temperatures, because of the low enthalpy of binding ($<10^3$ cm^{-1} = 3 kcal) and the appreciable entropy of association (-20 eu).[8] Thus, most of the triplets would be present as monomer in their experiments and, since the phosphorescence lifetimes are about the same, it would be very difficult to observe and identify dimer phosphorescence definitively. We suspect that the conclusions of Lim and Chakrabarti are not valid. Our findings are consistent with those of Kearns,[4] but it should be noted that dyes show excited dimer rather than excimer fluorescence. The failure of naphthalene to form a triplet excimer under our conditions suggests that the binding energy of this state is too small to compensate for the energy required to decrease intramolecular spacing to that of an excimer (3–3.2 Å). The instability of aromatic hydrocarbon triplet excimers relative to triplet monomers has been predicted recently by Lim.[11]

(11) A. K. Chandra and E. C. Lim, *J. Chem. Phys.*, **49**, 5066 (1968).

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Interaction of Nonconjugated Double Bonds

Sir:

The interaction of nonconjugated π-electron systems has attracted great theoretical and experimental interest.[1] It is clear that in neutral molecules experimental evidence for such interaction should be sought not in the total energy, but in spectral and ionization properties.[2] The most direct measure of this interaction is the difference in the ionization potentials of the interacting double bonds, relative to the ionization potentials of isolated, noninteracting systems. Through the technique of photoelectron spectroscopy[5] such measurements have become feasible and are now available for 1,4-cyclohexadiene, norbornadiene, and related molecules.[6] We wish to show here that two distinct symmetry-controlled mechanisms for interaction of π-electron systems, (1) direct through-space overlap and (2) through-bond or hyperconjugative interaction, may result in qualitatively divergent interaction patterns.

The model for dominant through-space interaction is norbornadiene (Figure 1). Such an interaction always places the positive overlap combination at lower energy, and accordingly the symmetric (with respect to plane 2) combinations of π and π^* levels should emerge below the antisymmetric. The SS–SA splitting is 0.43 eV in an extended Hückel calculation, much larger in a Hückel calculation,[1a] and 0.85 eV experimentally.[6]

Contrast the norbornadiene case with a model for optimal hyperconjugation, a planar 1,4-cyclohexadiene[7] (see Figure 2). We show in this figure only the σ orbitals which have π-type symmetry.[8] The SS double bond combination is destabilized by mixing with a CH_2 σ level. *The remarkable result is that the SS and SA levels are split by the hyperconjugative interaction in the opposite sense to the direct interaction.* The extended Hückel calculations for a planar model confirm the level ordering, and yield a splitting of 0.65 eV. The experimental result is 1.0 eV.[6] Of course the photoelectron spectrum does not tell us which level is lower, and in that sense confirmation of these predictions must await further physical studies.

We have also carried out "molecules in molecules" studies of the interaction of double bonds in these systems,[9] and these fully confirm the simple symmetry-based argument offered above.

An interesting level ordering reversal should be observed for bicyclo[2.2.2]octatriene *vs.* bullvalene (Figure 3). In the former the through-space interaction is dominant, leading to a splitting of the three π levels so that the more bonding degenerate e′ combination falls below the totally antibonding (between double bond units) a_2' level.[1a,10] In the case of bullvalene we construct the interaction between the three π levels and the Walsh orbitals of the cyclopropane ring.[10] The ordering of bonding π levels is clearly reversed, and extended Hückel calculations confirm this point.

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(1) (a) C. F. Wilcox, Jr., S. Winstein, and G. McMillan, *J. Amer. Chem. Soc.*, **82**, 5450 (1960); (b) P. Radlick and S. Winstein, *ibid.*, **85**, 344 (1963); K. G. Untch, *ibid.*, **85**, 345 (1965); W. R. Roth, *Ann.*, **671**, 10 (1964); W. R. Roth, W. B. Bang, P. Goebbel, R. L. Sass, R. B. Turner, and A. P. Yü, *J. Amer. Chem. Soc.*, **86**, 3178 (1964); S. Winstein and F. P. Lossing, *ibid.*, **86**, 4485 (1964); S. Winstein in "Aromaticity," Special Publication No. 21, The Chemical Society, London, 1967, p 5; (c) H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959); (d) R. C. Cookson, J. Henstock, and J. Hudec, *J. Amer. Chem. Soc.*, **88**, 1060 (1966).

(2) The situation differs markedly for charged species (ref 1b and 3) and diradicals (ref 4).

(3) M. J. Goldstein, *J. Amer. Chem. Soc.*, **89**, 6357 (1967).

(4) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).

(5) D. W. Turner, *Proc. Roy. Soc., A*, **307**, 15 (1968).

(6) P. Bishof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).

(7) The actual molecular geometry is slightly bent, with a dihedral angle of 159°: H. Oberhammer and S. H. Bauer, *J. Amer. Chem. Soc.*, **91**, 10 (1969). See also G. Dallinga and L. H. Toneman, *J. Mol. Struct.*, **1**, 117 (1967); E. W. Garbisch, Jr., and M. C. Griffith, *J. Amer. Chem. Soc.*, **90**, 3590 (1968); R. C. Lord, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., 1968, No. PHYS 74; A. D. Buckingham, E. E. Burnell, and C. A. de Lange, *Mol. Phys.*, **16**, 521 (1969).

(8) Figure 2 shows the interaction with the bonding σ CH_2 levels of π-type symmetry. In principle one should include the antibonding σ^* levels of the same symmetry type in this kind of interaction diagram. Our experience (R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968); R. Hoffmann, A. Imamura, and W. J. Hehre, *ibid.*, **90**, 1509 (1968)) has been that in hyperconjugative interactions mixing with the σ level is more important than that with σ^*. Two reasons for this emerge: (1) in calculations with overlap included the σ^* level is at very high energy; (2) overlap of adjacent p orbitals with σ is more efficient than with σ^*, since the latter has more nodes.

(9) E. Heilbronner and P. A. Straub, to be published.

(10) The argument here parallels that applied to the ordering of the cyclopropane orbitals in the Walsh model: A. D. Walsh, *Trans. Faraday Soc.*, **45**, 179 (1949).