cross sections were shown to be independent of energy above a few hundred electron volts up to 15 keV and should remain so over the range of electrons produced by Co^{60} γ rays. The argon L electron has about a 250-eV ionization potential as opposed to about 16 eV for the valence electron, so L ionization receives about 45% of the total energy absorbed by argon. In high argon mixtures, 40% of the methane converted goes to polymer; *i.e.*, $G(-\mathrm{CH_4}\text{ to polymer})/[G(-\mathrm{CH_4}\text{ to polymer}) + G(-\mathrm{CH_4}\text{ to ethane})] = 1.3/(1.3 + 2.0) = 0.40$. Thus our hypothesis does predict the experimental results.

In the case of methane, the lower relative cross section for carbon K ionization means this process receives approximately an estimated 4% of the energy absorbed.[12] In pure condensed methane $G(-\mathrm{CH_4}$ to ethane$) = 4.6$,[2,13] intermediate size products have $G(-\mathrm{CH_4}) = 0.3$,[2] and polymer is $G(-\mathrm{CH_4}) = 0.2$–0.3 (liquid and solid phase). Thus polymer accounts for about 5% of the G for methane lost in condensed-phase methane, a number which again correlates well with the energy going into inner shell ionization.

Another way of stating these correlations is that the ratio of energy going to argon L *vs.* carbon K ionization is about 11(45/4), which is the same as the ratio of G's for polymer made in high argon *vs.* high methane radiolysis.

In hot-atom chemistry Auger processes have been known to be important for a long time. The chemical consequences of nuclear isomeric transitions and internal conversion of γ rays have come to understanding in this way.[14,15] The search for inner-shell ionization effects is an old one, too, with some evidence of success,[12,15] but the present evidence emphasizes the possible differences between the effects of inner- and outer-shell ionization in radiation chemistry.

Of course as suggested earlier[2] the hydrogen-deficient positive ions which are rich in energy, CH_n^+ ($n = 0, 1, 2, 3$), may be the source of the polymer, and we must remember that 584-Å light (21-eV energy) which is of too low energy to make Auger electrons also gave polymer,[16] although in this case the polymer was less well characterized. Recently Olah and Schlosberg[17] have reported that the chain polymerization can run downhill energetically once $\mathrm{CH_3^+}$ is initially formed. The variation in polymer yield with the energy-absorbing material might be explained by an increase in the production of species such as $\mathrm{CH_3^+}$ when methane is ionized by charge transfer from argon ions.[18] However, in the dilute liquid solutions the predominant $\mathrm{Ar_2^+}$ ion[4] (recombination energy about 13.7 eV)[19] cannot deliver enough excitation energy to methane to produce many fragment ions like $\mathrm{CH_3^+}$.

In conclusion, the production of polymer in the dilute argon solutions gives another set of limiting conditions on the mechanism of polymerization of methane by ionizing radiation, and furthur experiments are under way.

---

(12) A. A. Ore, Proceedings of 3rd International Congress of Radiation Research, Cortina D'Ampezzo, 1966, p 54.

(13) H. A. Gillis, *J. Phys. Chem.*, **71**, 1089 (1967).

(14) (a) E. P. Cooper, *Phys. Rev.*, **61**, 1 (1942); (b) S. Wexler and T. Davies, *J. Chem. Phys.*, **20**, 1688 (1952); (c) A. R. Kazanjian and W. F. Libby, *ibid.*, **42**, 2778 (1964).

(15) R. L. Platzman, "Symposium on Radiobiology," J. J. Nickson, Ed., John Wiley and Sons, Inc., New York, N. Y., 1952, Chapter 7.

(16) C. A. Jensen and W. F. Libby, *J. Chem. Phys.*, in press.

(17) G. A. Olah and R. H. Schlosberg, *J. Am. Chem. Soc.*, **90**, 2726 (1968).

(18) (a) C. E. Melton, *J. Chem. Phys.*, **33**, 647 (1960); (b) R. W. Hummel, *Nature*, **192**, 1178 (1961).

(19) P. Kebarle, R. M. Haynes, and S. K. Searles, *J. Chem. Phys.*, **47**, 1684 (1967).

Spectroscopic Studies on the α-Phenylated Naphthalenes[1]

Arnold Zweig and James B. Gallivan

Contribution from the Chemical and Research Service Departments,
Central Research Division, American Cyanamid Company,
Stamford, Connecticut 06904. *Received May 8, 1968*

Abstract: The fluorescence and phosphorescence emission spectra of the six α-phenylnaphthalenes are described. On increased phenyl substitution bathochromic shifts are observed for both transitions, the phosphorescence lifetimes decrease, and the ratio of phosphorescence to fluorescence diminishes. The energy available from triplet-triplet annihilation is reduced more rapidly than the energy of the lowest singlet state as successive phenyls are added to naphthalene. If an analogous relationship exists for tetracene and the phenylated tetracenes, then T–T annihilation in rubrene (5,6,11,12-tetraphenyltetracene) will fail to generate the fluorescent singlet state because of an energy insufficiency of ~5 kcal/mole. The significance of these results to the mechanism of electron-transfer luminescence is discussed. The properties of all of the α-phenylnaphthalenes, including their nmr spectra, are best accounted for by pπ–pπ overlap of nonperpendicular adjacent orbitals rather than by spiroconjugative interaction.

Polycyclic aromatic compounds are often both fluorescent and phosphorescent. These characteristic properties are invaluable tools for elucidating other photophysical and photochemical behavior. When such molecules are multiply substituted by phenyl groups to form compounds such as rubrene (5,6,11,12-tetraphenyltetracene) and 9,10-diphenylanthracene, the products exhibit strong fluorescence, but no phosphorescence is observed. The usually intense fluorescence of such compounds has been explored and utilized, but the

---

(1) (a) Cumulative Influence of Conjugated Substituents on the π-System Properties of Aromatic Hydrocarbons. XIII; (b) part XII: A. Zweig, J. E. Lancaster, and M. T. Neglia, *Tetrahedron*, **23**, 2577 (1967).

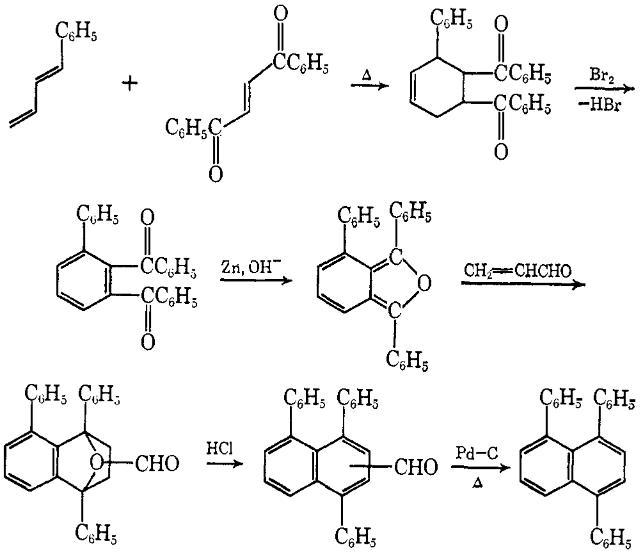
inability to detect phosphorescence has prevented proper characterization of their lowest triplet levels. To gain insight into how the triplet state energy changes when multiple phenyl substitution occurs, we have studied the effect of successive α-phenyl substitution on the emissive properties of naphthalene. Examination of the properties of a complete set of consecutively substituted molecules may provide valuable insight into the nature of their electronic structure and may offer an experimental choice between proposed theoretical models.[2]

The α-phenylnaphthalenes are a series of six compounds, five of which have been reported previously. The parent, naphthalene, is both fluorescent and phosphorescent having a ϕ_P/ϕ_F ratio of 0.12 in hydrocarbon glass at 77°K. The most highly phenylated member of the series, 1,4,5,8-tetraphenylnaphthalene, was previously reported to be fluorescent but not detectably phosphorescent under the experimental conditions employed.[3]

We report here the fluorescence and phosphorescence results for all of the α-phenylnaphthalenes including the 1,4,5,8- tetraphenylnaphthalene. Weak short-lived phosphorescence from the latter was observed under intense irradiation conditions. In addition we report nmr and uv absorption data for those compounds of the series which had not been examined previously.

Preparation of Compounds. All of the α-phenylnaphthalenes were known previously with the exception of 1,4,5-triphenylnaphthalene. The latter was prepared by an adaptation of one of the syntheses of 1,4,5,8-tetraphenylnaphthalene.[4,5] As shown in Chart I, the Diels–Alder adduct of 1-phenylbutadiene and 1,2-dibenzoylethylene was aromatized and the product was cyclized to give 1,3,4-triphenylisobenzofuran. Diels–Alder condensation of this isobenzofuran with acrolein gave a crude fraction of adducts which was not separated but was directly treated with anhydrous hydrochloric acid to give (presumably) a mixture of 1,4,5-triphenylnaphthalene-2 (and -3-) carboxaldehyde. Crystallization of the product gave a single isomeric carboxaldehyde sharply melting at 197–198°.[6,7] Decarbonylation of this compound with palladium on charcoal gave the desired 1,4,5-triphenylnaphthalene.

Chart I



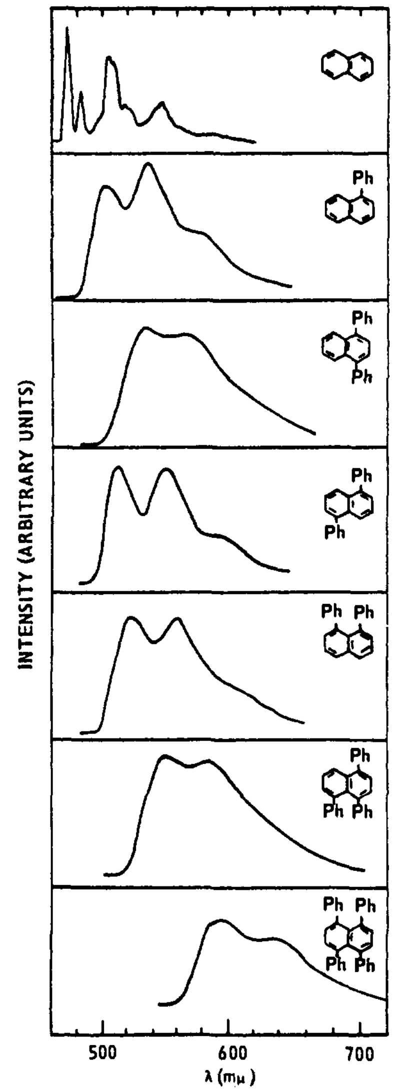


Figure 1. Phosphorescence emission spectra of naphthalene and the α-phenylnaphthalenes in 3-methylpentane at 77°K.

Emission Spectroscopy. Both the fluorescence and phosphorescence emission spectra of 10^{-3} to 10^{-4} M solutions of the α-phenylnaphthalenes were obtained in a 3-methylpentane (3MP) glass at 77°K. As can be seen in Figure 1 the phosphorescence spectra undergo bathochromic shifts and loss of vibrational structure as successive phenyls are added. The fluorescence spectra showed similar effects, and the loss of fine structure was even more pronounced. Because of this lack of vibrational structure in the phenylated naphthalenes the triplet energies in Table I refer to wavelengths corresponding to 10% of the phosphorescence peak intensity. The same procedure was followed in determining the singlet energies from the fluorescence spectra. Com-

---

(2) A. Zweig and J. E. Lehnsen, *J. Am. Chem. Soc.*, **87**, 2647 (1965).

(3) A. Zweig, A. K. Hoffmann, D. L. Maricle, and A. H. Maurer, *ibid.*, **90**, 261 (1968).

(4) E. D. Bergmann, S. Blumberg, P. Bracha, and S. Epstein, *Tetrahedron*, **20**, 195 (1964).

(5) C. Dufraisse and Y. Lepage, *Compt. Rend.*, **258**, 1507 (1964).

(6) If acrolein undergoes a concerted but asymmetric Diels–Alder reaction, with one bond closure occurring faster than the other,[7] then the transition state resulting in the formation of 1,4,5-triphenylnaphthalene-3-carboxaldehyde will be of lower energy than that which would form the corresponding 2-carboxaldehyde.

(7) R. B. Woodward and T. J. Katz, *Tetrahedron*, **5**, 70 (1959).

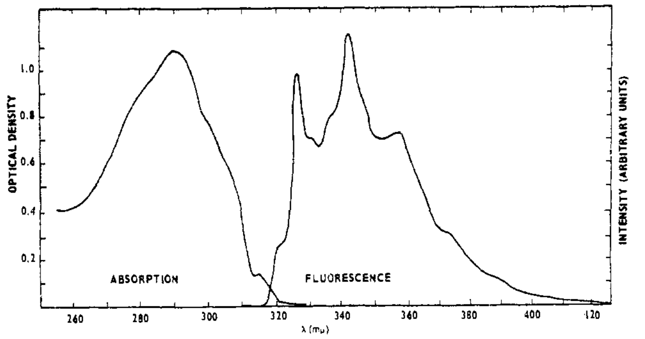


Figure 2. Normal uv absorption and fluorescence spectra of α-phenylnaphthalene in 3-methylpentane at 77°K.

Table I. Emission Data for Naphthalene and the α-Phenylnaphthalenes at 77°K in 3-Methylpentane

	Phosphorescence			Fluorescence	
Naphthalene	$\lambda(E_T)$, mμ	τ_m, sec	ϕ_P/ϕ_F	$\lambda(E_S)$, mμ	λ_{max}, mμ
Unsubstituted	472	2.4	0.12	316	321
1-Phenyl-	484	1.20	0.11	322	327
1,4-Diphenyl-	504	0.80	0.06	338	368
1,5-Diphenyl-	494	1.30	0.08	328	357
1,8-Diphenyl-	498	0.73	0.05	329	355
1,4,5-Triphenyl-	522	0.48	0.03	348	379
1,4,5,8-Tetraphenyl-	565	0.055	<0.01	377	412

parison of the low-temperature fluorescence and absorption spectra for α-phenylnaphthalene for which a partially resolved electronic origin was observed (Figure 2) indicates that this is a realistic estimate of the energy, and it has the advantage of minimizing the relative error in intercompound comparisons. The phosphorescence and singlet–triplet absorption spectra of α-phenylnaphthalene reported by Marchetti and Kearns[8] indicate that such a procedure is also realistic in assigning triplet-state energies.

Only in the 1,8-diphenylnaphthalene was there any indication of impurity emission. For this compound, several weak phosphorescence bands were observed at higher energies than the principal phosphorescence emission. The impurity phosphorescence had a lifetime less than half that of the main emission, and the weak bands were easily separated from the relatively intense 1,8-diphenylnaphthalene phosphorescence. There was no evidence of changing emission characteristics during the course of the experiments—or after more extended irradiation at 77°K.

The delayed emission from 1,4,5,8-tetraphenylnaphthalene was initially seen in EEET (ether, ethyl iodide, ethanol, and toluene—2:2:1:1) and *n*-butyl bromide glasses when the sample was excited by intense uv light from a 1000-W xenon arc after passing through a nominal monochromator (6-mm slits centered on 3500 Å). Under these conditions the phosphorescence peaked at 586 mμ in EEET and 590 mμ in *n*-butyl bromide. In 3MP, with the same source, the emission was much weaker but had essentially the same spectral distribution (Figure 1). In this matrix the peak emission was at 594 mμ and the lifetime was measured as 0.055 sec. As the spectral shape of the phosphorescence from this compound resembled that of the other phenylnaphthalenes, and as the phosphorescence lifetime and ϕ_P/ϕ_F ratio were both in anticipated regions, there is little reason to suspect that it may be due to an impurity.

The mean phosphorescence lifetimes and the ϕ_P/ϕ_F ratios for all the α-phenylnaphthalenes are reported in Table I.

Nmr Spectra. The nmr spectra of α-phenylnaphthalene, 1,7-diphenylnaphthalene, and 1,8-diphenylnaphthalene were reported by House and coworkers[9] who found an upfield shift of about 0.5 ppm for the ten phenyl protons of 1,8-diphenylnaphthalene relative to the phenyl protons in the others. The shift was interpreted as being the result of having each set of phenyl protons shielded by an adjacent parallel benzene ring in the ground state. A similar upfield shift was also observed for the phenyl protons of 1,4,5,8-tetraphenylnaphthalene, and a similar interpretation was made.[10]

An examination of the proton nmr spectra of 1,4-diphenylnaphthalene, 1,5-diphenylnaphthalene, and 1,4,-5-triphenylnaphthalene is very revealing. The triphenyl derivative shows an upfield shift for ten protons which is absent in the first two while a downfield chemical shift was observed for two protons in the first two compounds and for one proton in the last. These downfield shifts can be assigned to the protons *peri* to the phenyl substituent.[1b] Table II summarizes the nmr data now available for the α-phenylnaphthalenes.

Discussion

Our primary interest in the emission properties of this series of compounds was to see how the first singlet and triplet energies changed with increased numbers of phenyl substituents. Triplet–triplet annihilation to produce the fluorescent S_1 state in rubrene has been postulated as a possible explanation of its emission under certain kinds of electrochemical stimulation.[11] Unfortunately, the energy of T_1 of rubrene has not been measured experimentally.[12] The first triplet energy level of the parent unphenylated tetracene (10,250 cm^{-1}) just fails to reach tetracene S_1 (20,990 cm^{-1}) by T–T annihilation.[13] It is not at all certain whether T_1–T_1 annihilation to produce S_1 would be more or less favorable in the tetraphenylated compound, rubrene.

To possibly gain some insight into what may happen in the tetracene–rubrene series and to gain further understanding of the phenylated napthalenes themselves, the analysis in Table III was made. The first column reports the singlet-state energies in kilokaisers (kK), and the second column shows the corresponding phosphorescence energies. It is apparent in this series that S_1 is exceeded by about 10 kK (28.6 kcal/mole) following T–T annihilation and the increment between 2T and S_1

---

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

[9] H. O. House, R. W. Magin, and H. W. Thompson, *J. Org. Chem.*, **28**, 2403 (1963).

[10] M. Rabinovitz, I. Agranat, and E. D. Bergmann, *Tetrahedron Letters*, 4133 (1965).

[11] J. Chang, D. M. Hercules, and D. K. Roe, *Electrochem. Acta*, **13**, 1197 (1968); D. L. Maricle and A. Maurer, *J. Am. Chem. Soc.*, **89**, 188 (1967).

[12] The combination of high melting point, low solubility, and photooxidizability has made the purification of rubrene a nasty matter. The reliable observation of rubrene phosphorescence has been frustrated by doubtful purity, low solubility, and a probable low emission intensity. Moreover, such emission would be expected to be short lived (milliseconds) and in the near-infrared (>1 μ) where detection is difficult due to greatly decreased sensitivity of available detectors.

[13] S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, **40**, 507 (1964); also see C. A. Parker, *Advan. Photochem.*, **2**, 370 (1964).

Table II. Nmr and Uv Spectral Data for the α-Phenylnaphthalenes

	Nmr data[a]			Uv data[b]	
Compound	Naphthyl protons	Phenyl protons	Ref	λ_{max}, mμ (log ε)	Ref
1-Phenylnaphthalene	7.4–8.0[d]	7.38	9	288 (4.03) 226 (4.80)	10
1,4-Diphenylnaphthalene	$H_{2,3}$ 7.38 $H_{6,7}$ 7.34 } A_2B_2 $H_{5,8}$ 7.89 }	7.44	*c*	300 (4.20) 231 (4.66)	9
1,5-Diphenylnaphthalene	$H_{4,8}$ 7.2–7.6[d]	7.2–7.6[d]	*c*	297 (4.17) 228 (4.68)	9
1,8-Diphenylnaphthalene	$H_{(2)}$ at 7.28, 7.82, 7.43[e]	6.85	9	300 (4.06) 235.5 (4.73)	9
1,4,5-Triphenylnaphthalene	H_8 8.25 $H_{(4)}$ 7.2–7.6[d]	6.7–7.1[d] (10) 7.2–7.6[d] (5)	*c*	312 (4.23) 240 (4.71) 217 sh (4.64)	*c*
1,4,5,8-Tetraphenylnaphthalene	$H_{2,3,6,7}$ 7.20	$H_{(4)}$ 7.00 $H_{(16)}$ 6.77	10	334 (4.18) 248 (4.50)	10

[a] In cycles/second from tetramethylsilane in CCl_4, except 1,4,5,8-tetraphenylnaphthalene in $CDCl_3$. [b] At 25° in ethanol except 1-phenylnaphthalene and 1,4,5,8-tetraphenylnaphthalene in cyclohexane. [c] This work. [d] Range of an incompletely resolved multiplet. [e] Centers of multiplets, complete assignment not made.

Table III. Relative Changes in Singlet and Triplet Energies of the α-Phenylnaphthalenes

Compound	Fluorescence energy (S_1), kK	Phosphorescence energy (T_1), kK	$2T_1 - S_1$, kK	$(2T_1 - S_1) - (2T_1 - S_1)$(naph), kK
Naphthalene	31.65	21.19	10.73	0.00
1-Phenylnaphthalene	31.06	20.66	10.26	−0.47
1,4-Diphenylnaphthalene	29.59	19.84	10.09	−0.64
1,5-Diphenylnaphthalene	30.49	20.24	9.99	−0.74
1,8-Diphenylnaphthalene	30.40	20.08	9.76	−0.97
1,4,5-Triphenylnaphthalene	28.74	19.16	9.58	−1.15
1,4,5,8-Tetraphenylnaphthalene	26.53	17.70	8.87	−1.86

decreases with increasing phenylation. The largest decrease in this increment relative to naphthalene (−1.86 kK − 5 kcal/mole) is observed for 1,4,5,8-tetraphenylnaphthalene. It should be noted that the average for the three diphenylnaphthalenes falls between the mono- and trisubstituted derivatives in increasing the increment between $2T_1$ and S_1. If an analogous relationship holds between tetracene and its phenylated derivatives up to rubrene, then T–T annihilation of the latter will fail by more than 5 kcal/mole in reaching rubrene S_1. On the basis of this analysis it is seen that the rubrene fluorescence emission produced under electron-transfer conditions cannot be a result of the triplet–triplet annihilation process!

The trend of the triplet lifetimes of the α-phenylnaphthalenes also bears on the mechanism of electron-transfer luminescence. The observed phosphorescence lifetime decreases by 50 times on going from naphthalene to its α-tetraphenylated derivative. This measured value in a rigid glass at low temperature is the sum of two independent first-order decay processes: a radiative process (the phosphorescence) and a nonradiative process. It has been suggested[14] that the radiative rate constant is ~30 sec^{-1} for all aromatic hydrocarbons. Thus the sharp decrease in phosphorescence lifetime on phenylation can be ascribed primarily to an increase in the unimolecular nonradiative decay process. Such a relative decrease is anticipated since the phenyl substituents will significantly increase the number of vibrational degrees of freedom, and it may reasonably be expected that the relative lifetimes will remain the same at room temperature. Thus the triplet lifetimes of the brightest electron-transfer chemiluminescence emitters (all highly phenylated) are among the shortest. While this fact seems to mitigate against the T–T mechanism for emission, it may not be controlling since the trends of other properties connected with emission may be more than sufficient to counteract it.

The nature of the electronic interactions which produce the bathochromic shifts in the absorption and emission spectra of the phenylated naphthalenes requires additional comment. The shift in absorption spectra was ascribed by Jaffé and Chalvet[15] to a type of interaction later termed spiroconjugation.[16] This interaction is strongest when two mutually perpendicular π-electronic systems have molecular orbitals which, in addition to their own essential nodal plane (the nodal plane of the atomic p orbitals from which the molecular orbitals are derived), have a nodal plane coincidental with the essential nodal plane of the other portion of the molecule. This arises when the group orbitals are antisymmetric with respect to each others essential nodal plane and results in the group orbitals interacting in the ways shown in Figure 3. Thus the formerly independent group orbitals can combine into a lower energy bonding arrangement (A) and a higher energy antibonding arrangement (B).

While this spiroconjugative effect is significant in the spirenes,[16,17] there are a number of reasons to believe that it is not responsible for the shifts observed here. For one the distance between the possible spirointeracting orbitals (2,6 on the phenyl and 2,9 on the naph-

---

(14) W. Siebrand, *J. Chem. Phys*, **47**, 2411 (1967).

(15) H. H. Jaffé and O. Chalvet, *J. Am. Chem. Soc.*, **85**, 1561 (1963).

(16) H. E. Simmons and T. Fukunaga, *ibid.*, **89**, 5208 (1967).

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

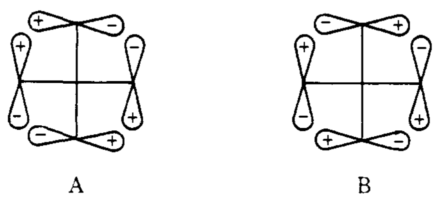


Figure 3. Interactions of antisymmetric perpendicular π-electronic systems with nodal planes coincidental with each others essential nodal planes: (A) attractive, (B) repulsive.

thyl) is about 1.4 Å further than in the spirenes; hence the orbital overlap must be much smaller. In addition, the highest filled and lowest unfilled orbitals of the naphthalene portion of the molecule are *not* antisymmetric with respect to the essential plane of the perpendicular α-phenyl substituents. This also has the effect of very sharply decreasing spiroconjugative overlap. Finally, the spiroconjugative effect does not predict a bathochromic shift in absorption spectra caused by *p*-methoxy substituents on the phenyls of some related compounds.[18] Since the *para* position is at the node of the antisymmetric benzene orbital, it should have no direct effect on the electronic structure of the molecule to which the phenyl is attached, and any indirect effect would surely be very small.

If the α-phenyl groups are not perfectly perpendicular to the naphthalene, then there is no need to invoke the spiroconjugative effect. Steric strain certainly precludes a fully planar situation in the ground state; however, if the *peri*-phenyl groups remain parallel to each other but only 30° out of perpendicular to the naphthalene ring, the exchange integral between p orbitals of the phenyl and naphthyl groups at the attached positions will be $0.134B_{cc}$,[19] very much larger than anything possible through spiroconjugation. It should be noted that this model is not in disagreement with the nmr data since the *peri*-phenyl substituents remain parallel.

Experimental Section

Spectroscopic. The luminescence spectrometer, low-temperature cell, and methods of solvent purification have all been described in the literature.[20] To observe the fluorescence from naphthalene and 1-phenylnaphthalene without interference from scattered exciting light, it was necessary to excite the samples at 285 instead of 313 mμ. For this purpose a 1000-W xenon lamp was used instead of the 200-W mercury lamp generally employed for excitation purposes. To observe phosphorescence from 1,4,5,8-tetraphenylnaphthalene in 3MP, it was necessary to use essentially the entire uv output of the xenon arc, as the excitation monochromator was set at 350 mμ and the slits opened to 6 mm. For comparison sake, all samples except the 1,4,5,8-tetraphenylnaphthalene were measured at spectra slit widths of $\sim$50 cm^{-1}. It was necessary to use an $\sim$100-cm^{-1} slit width to observe the phosphorescence from the tetraphenyl derivative in 3-methylpentane.

To determine ϕ_P/ϕ_F ratios, the spectrometer was calibrated to correct for photomultiplier (EMI-9558Q) sensitivity as a function of wavelength. Independent calibrations using a NBS (No. 156) quartz–iodine lamp and a Quantalumen (Model 141) tungsten lamp agreed to within ±5% in the 400–750-mμ region. In the uv region where agreement was not as good, the calibration based on the higher color temperature (quartz–iodine) lamp was used. A computer program was used which corrected for the changes in phototube sensitivity and gave corrected fluorescence and phosphorescence spectra on an energy scale. The areas under these corrected curves were taken to give the ϕ_P/ϕ_F ratios. No attempts were made to determine absolute values of ϕ_P or ϕ_F. The phosphorescence lifetimes were measured by a conventional technique. The spectrometer was set at the λ_{max} of the various bands, the signal was displayed on an oscilloscope, and a photograph was taken of the decay of the signal *vs.* time following extinction of the exciting light.

Synthesis. 3-Phenyl-4,5-dibenzoylcyclohexene. A mixture of 19.5 g (0.15 mole) of freshly distilled 1-phenylbutadiene[21] and 32.0 g (0.136 mol) of *trans*-1,2-dibenzoylethylene (Eastman Kodak Co.) in 300 ml of methanol was refluxed for 18 hr. The hot reaction product was filtered and the solvent was removed to give a yellow glass. One crystallization from ethanol gave 26.5 g (53%) of a white compound, mp 116–118°. Repeated crystallization from methanol gave an analytical sample, mp 120–121°, of 3-phenyl-4,5-dibenzoylcyclohexene.

Anal. Calcd for $C_{26}H_{22}O_2$: C, 85.21; H, 6.05. Found: C, 85.19; H, 5.90.

2,3-Dibenzoylbiphenyl. A solution of 23.0 g (0.063 mole) of 3-phenyl-4,5-dibenzoylcyclohexene in 500 ml of chloroform was heated to reflux, and 40.0 g (0.0125 mole) of bromine in 120 ml of chloroform was added dropwise. The reaction mixture was heated until gas (HBr) evolution ceased. The solvent was removed under vacuum and 200 ml of methanol was added to the residual oil which then crystallized. Filtration gave 11.5 g (50%) of 2,3-dibenzoylbiphenyl, mp 170–172°. Repeated crystallization from methanol gave mp 173–174°.

Anal. Calcd for $C_{20}H_{18}O_2$: C, 86.16; H, 5.01. Found: C, 85.76; H, 4.86.

1,4,5-Triphenylnaphthalene. To a refluxing solution of 9.3 g (0.026 mole) of 2,3-dibenzoylbiphenyl and 9.3 g (0.23 mole) of sodium hydroxide in 225 ml of absolute ethanol was added 10.0 g (0.15 g-atom) of activated zinc dust. The zinc was activated by washing successively with 1 *N* sodium hydroxide, water, and ethanol. The reaction mixture was stirred and refluxed under nitrogen for 1 hr and then filtered hot into 225 ml of glacial acetic acid. Addition of 150 ml of water caused a flocculent yellow precipitate to form. Filtration and air-drying in the dark gave 3.1 g of crude, intensely fluorescent, 1,3,4-triphenylisobenzofuran, mp *ca.* 130–150°. Without further purification, this substance was dissolved in 75 ml of benzene, and 2.5 ml of freshly redistilled acrolein was added. The mixture was refluxed for 1 hr, and the resulting material was evaporated to dryness and taken up in methanol. A yellow solution was obtained together with some crystalline material. Filtered and dried, the crystalline material proved by melting point (172°) and ir to be 2,3-dibenzoylbiphenyl. The yellow solution was evaporated to dryness and taken up in 10 ml of glacial acetic acid which was then bubbled with anhydrous hydrochloric acid for 1 hr. The resulting yellow crystalline substance was filtered and dried. Recrystallization from *n*-heptane gave 0.40 g of yellow solid, mp 197–198°, of 1,4,5-triphenylnaphthalene-2- (or -3-) carboxaldehyde.

Anal. Calcd for $C_{29}H_{29}O$: C, 90.59; H, 5.24. Found: C, 90.57; H, 5.18.

Into a test tube was placed 0.20 g (0.00052 mole) of 1,3,4-triphenylnaphthalene-2- (or -3-) carboxaldehyde together with 0.02 g of 10% palladium on charcoal. The mixture was heated to 290–300° for 5 hr, then cooled, dissolved in 10 ml of benzene, and filtered. The benzene was removed and the resulting gum was taken up in 10 ml of hot heptane. On cooling and scratching a crystalline material formed. Repeated recrystallization from heptane gave 0.1 g of 1,4,5-triphenylnaphthalene, constant mp 138–139°.

Anal. Calcd for $C_{28}H_{20}$: C, 94.34; H, 5.66. Found: C, 94.18; H, 5.64.

Acknowledgment. We thank H. O. House for a sample of 1,8-diphenylnaphthalene and W. Henderson, Jr., for the 1,5-diphenylnaphthalene. We also thank Dr. J. E. Lancaster for a discussion and for obtaining the nmr spectra.

---

[18] A. Zweig, G. Metzler, A. Maurer, and B. G. Roberts, *J. Am. Chem. Soc.*, **89**, 4091 (1967).

[19] A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961.

[20] J. B. Gallivan, J. S. Brinen, and J. G. Koren, *J. Mol. Spectry.*, **26**, 24 (1968).

[21] O. Grummitt and E. I. Becker, "Organic Syntheses," Coll. Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1963, p 771.