oxygen atom (O3, IV). Bil'kis et al.[17] characterized the cation and anion radicals of some substituted phenoxazones as the nitrogen atom (N10) being the radical site for the anion radical (II) and an oxygen (O5, V) being the radical site for the cation radical. Because of Bil'kis' conclusion, we assigned the radical site of AMD to the nitrogen atom (N10, II). Compound **3**, however, has an additional reducible substituent besides the quinonimine nucleus, namely, the nitro group. By brief analysis of the hyperfine splitting pattern of the radical, the radical site also seems to be located on N10. The examination of substituent effects on redox potential is being examined at present.

$NaBH_4$ is the strongest among the reducing agents we used for this study. Anion radical formation can be effected by careful addition of $NaBH_4$; however, excess reagent tends to enhance further reduction to the dianion.[18] With respect to the hypsochromic modification of AMD, it has been reported that dilute alkaline solutions cause a cleavage of the phenoxazone ring system and associated disappearance of color.[9] In this instance, the water content of the Me_2SO may lead to formation of a strongly basic reaction product as observed by Schlesinger et al.[19] ($NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2$) which could then cause ring cleavage. $NaBH_4$ reduction, however, yields a product with a λ_{max} of 362 nm and no definitive isosbestic point. These differences indicate that the integrity of the fused ring system is preserved during $NaBH_4$ reduction.

Among common biochemical reducing agents such as NADPH, cysteine, ascorbic acid, and glutathione, only NADPH is effective as a cofactor in the enzymatic reduction of anthraquinones.[20] In our experiments, however, NADPH is not as effective for AMD generation of free radicals under similar conditions.[7] This tends to suggest that phenoxazone is a weaker oxidant than anthracyclines.

Rat liver NADPH cytochrome P-450 reductase catalyzed the single-electron reduction of quinone antibiotics to a semiquinone free-radical state with NADPH as the electron donor.[20] After chemical reductive activation, adriamycin and daunorubicin cause DNA breakage and damage.[21] We find that rat liver microsomes and NADPH cytochrome P-450 reductase catalyzed NADPH-dependent oxygen consumption with AMD and produced an AMD free radical,[7] which is similar to anthracycline drugs. Since AMD is known to cause DNA damage in cells, the free radical form of AMD produced chemically or enzymatically may be the means by which this damage is produced. This action may be the source of pharmacologic activity and toxicity of these drugs. In order to understand more quantitatively the reaction mechanism for reduction and free radical formation, we are presently engaged in electrochemical studies of AMD and its analogues.

Experimental Section

AMD was obtained from the Drug Development Branch, DCT, NCI, Bethesda, MD. 2-Amino-3-phenoxazone (**2**) and 1,2,4-trichloro-7-nitro-3-phenoxazone (**3**) were synthesized according to published methods[22,23] and were purified by preparative TLC (Chart I).

Preparative silica gel G plates (Merck, Darmstadt) were activated by being heated at 130 °C for 30 min. One to two milliliters of a concentrated tetrahydrofuran (THF) solution of **2** or **3** was applied in a streak and dried in air. Compound **2** was developed in ethyl acetate/chloroform (1:1) and **3** in chloroform/methanol/acetic acid (200:4:5). The band of interest was removed and eluted with THF to yield pure product. UV-visible absorption spectra were obtained on an Aminco DW-2 UV-visible spectrometer with a scan speed of 20 nm/s. Infrared spectra were obtained from a Perkin-Elmer 197 infrared spectrophotometer in a 0.2-mm sodium chloride cell with THF as solvent. EPR spectra were acquired at room temperature on a Varion E-9 spectrometer with 100-KHz field modulation and a flat sample cell. The g values were calculated against a strong pitch as standard. Oxygen was purged off with bubbling nitrogen gas for 5 min in order to get the EPR spectra and absorption spectra.

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One-Electron Photooxidation of Carbazole in the Presence of Carbon Tetrachloride

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It has been shown that aromatic amine molecules like indole interact in their triplet excited states with halocarbon molecules through normal external spin-orbital coupling or by complexation when chlorine atoms were part of the halocarbon molecule.[1] Similar results have recently been obtained with carbazole except that the interaction with halocarbons is much less than that with indole.[2] Ground-state charge-transfer complexes between carbazole derivatives and strong electron-acceptor molecules like chloranil and tetracyanoethylene have been observed.[3] On the other hand, an exciplex mechanism for the quenching of singlet excited states of aliphatic ketones[4] and aromatic hydrocarbons[5-7] by carbon tetrachloride has been proposed. Even though we were unable to show any evidences of ground-state complexation between carbazole and carbon tetrachloride, a good correlation was obtained between the fluorescence quenching rate constants and the quenchers half-wave reduction potentials ($E_{1/2}$), suggesting that the quenching mechanism involved an electron trasfer from the excited singlet carbazole to the halocarbon molecules.[8] Whether an excited triplet state of carbazole might play a role or not in the primary photochemical electron-transfer event is not ruled out at the moment.[9,10] We report here on the photochemical aspect of the problem which confirms the mechanism discussed above.

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Results and Discussion

We found that the main products obtained from the photochemical reaction of carbazole with CCl_4 in ethanol as a solvent are 1-(carboethoxy)carbazole (1) and 3-(carboethoxy)carbazole (2). In 3-methylpentane (3-MP) as a solvent *N*-(trichloroethylene)carbazole (3) has been mainly obtained. In pure CCl_4 saturated with ammonia gas, *N,N'*-dicarbazyl (4) and *N*-cyanocarbazole (5) have been obtained. In each of the reaction media studied, hexachloroethane was also found to be formed.

Electronic excitation of carbazole (C) in the presence of CCl_4 has then been found to initiate photochemical reactions. The large number of products formed along with the quantity of each depends on the reaction medium. This is an indication of the occurrence of complex secondary photochemical reactions in the carbazole–CCl_4 system. On the basis of the well-known photophysical results[4-8] and also on the photochemical reaction products obtained, the primary photophysical and photochemical reactions shown in eq 1–6 might be written.

$$C + h\nu \rightarrow {}^1C^* \quad (1)$$

$${}^1C^* + CCl_4 \rightsquigarrow {}^3C^* + CCl_4 \quad (2)$$

$${}^1C^* \rightarrow C + h\nu_F \quad (3)$$

$${}^1C^* + CCl_4 \rightsquigarrow {}^1(C^{\delta+}...CCl_4^{\delta-})^*_{solv} \quad (4)$$

$${}^1(C^{\delta+}...CCl_4^{\delta-})^*_{solv} \rightsquigarrow {}^3C^* + CCl_4 \rightsquigarrow {}^1C^* + CCl_4 \rightsquigarrow C + CCl_4 \quad (5)$$

$${}^1(C^{\delta+}...CCl_4^{\delta-})^*_{solv} \rightsquigarrow \{C^{+\cdot}\ Cl^-\ \dot{C}Cl_3\}_{solv} \quad (6)$$

We suggest that the electron transfer from carbazole to the CCl_4 molecule is followed by a heterolytic dissociation of a C–Cl bond, giving rise to the possible primary products in the solvent cage (eq 6). The presence of hexachloroethane in the reaction media is presumably connected with reaction 6 followed by recombination of trichloromethyl radicals (eq 7).

$$2\dot{C}Cl_3 \rightarrow C_2Cl_6 \quad (7)$$

The secondary products obtained and identified along with the data published[11-20] allow us to propose the mechanism of transformation of the carbazole radical cation in the solvent cage shown in Scheme I.

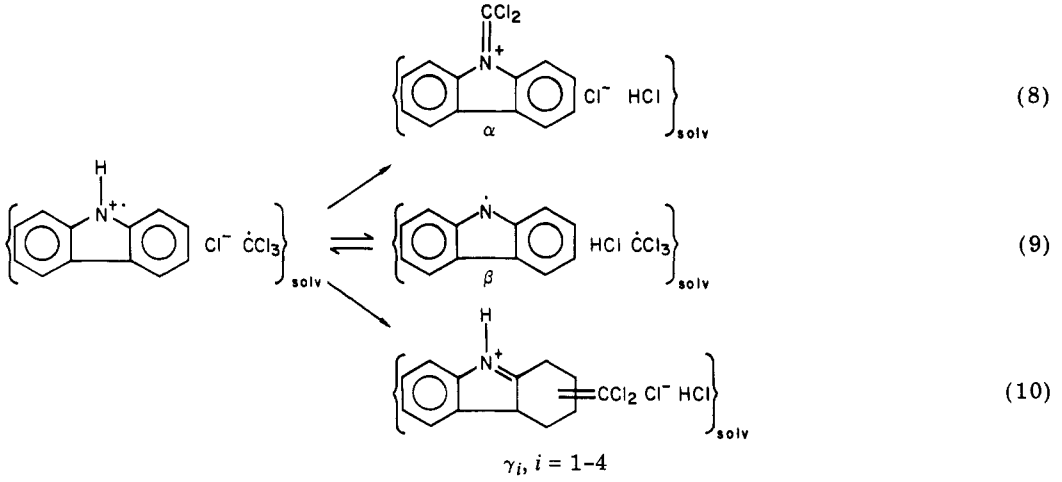
The electron densities calculated for the carbazole molecule show that among a variety of mesomeric structures of the radical cation, the 1, 3, 6, 8, and 9 (N) positions are likely to be favored.[11,12] This was later confirmed by the analysis of the electrochemical oxidation products of carbazole and its substituted derivatives.[12,13] Radical recombination reactions 8 and 10 in the solvent cage then become very probable, giving the intermediate ionic products α and γ_i (mainly with $i = 1$ or 3). The presence of chlorine ion in the solvent cage makes possible the transformation of the radical cation of carbazole to carbazyl radical β. But since the N–H and H–Cl bond energies are nearly the same at 431 kJ mol^{-1},[14] reaction 9 is probably reversible.[15]

The secondary reaction mechanism in the solvent cage proposed above is in partial agreement with earlier photochemical invesigations on aromatic amine–CCl_4 systems.[16-20] It seems that the probability of transformation of the α, β, and γ_i intermediates depends strongly on the nature of the reaction medium.

Indeed we have evidence that radical β is formed in higher yield in basic media like NH_3 since *N,N'*-dicarbazyl has been obtained (eq 11).

Probably that the process of removing the hydrochloride

Scheme I



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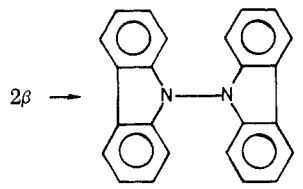

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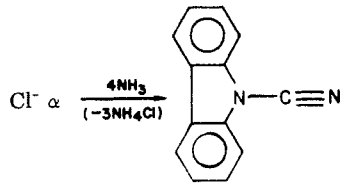
from the reaction medium promotes the formation of the β radicals and their out of cage reaction.

Intermediate α might be the precursor of *N*-cyanocarbazole (eq 12) and *N*-(trichloroethylene)carbazole (eq 13).



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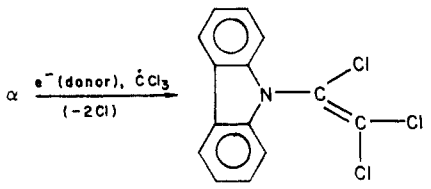

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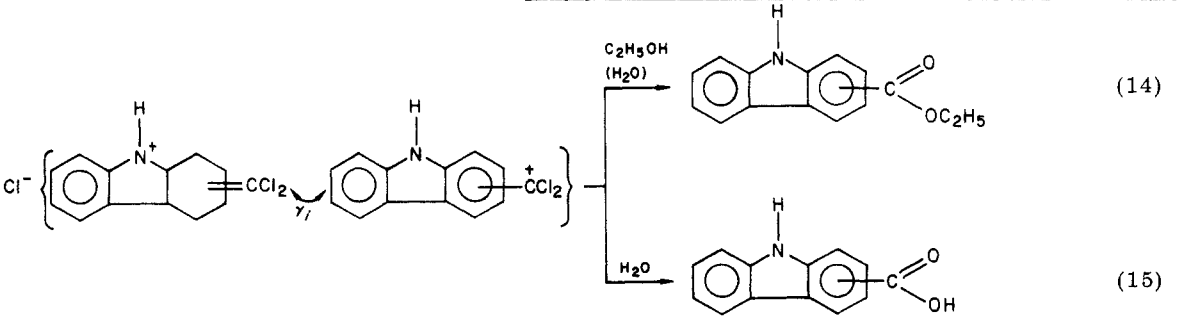
Reaction 12 accounts for the formation of *N*-cyanocarbazole. This reaction occurs only in the case when NH_3 is present in the reaction medium. On the other hand the formation of compound **3** is more probable in a nonpolar medium like 3-MP which favors radical reactions, but it is also present in other media. The mechanism by which this compound **3** is formed is not known exactly and this will require further studies. According to reaction 13, the first step might be the reduction of the α cation to the corresponding radical in the presence of an electron donor (an excited carbazole molecule, for example) followed by out of cage reactions.

The γ_i intermediates (eq 10) are very reactive in the presence of ethanol or water. In "CCl_4–C_2H_5OH" they undergo further transformations according to eq 14 to give a mixture of (carboethoxy)carbazoles, mainly **1** and **2**.



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In "CCl_4–3-MP" as well as in pure CCl_4, intermediate γ_i reveals significant stability in the reaction medium. However, during further manipulation of the photolysis products in contact with atmospheric water, they are easily hydrolyzed to the corresponding carboxylic acids (eq 15).

Irradiation of carbazole solution in pure CCl_4 gives rise to the intermediates α and γ_i in high yields. If we add ethanol to the photolysis solution, (carboethoxy)carbazoles are among the products. It indicates that reaction 14 occurs. But if we saturate this irradiated solution with NH_3 gas, *N*-cyanocarbazole is among the products according to reaction 12.

These photochemical results strongly support the electron-transfer mechanism used to explain the fluorescence quenching of carbazole by the halocarbons.[8] They also depict new possibilities of applications of electron acceptors like CCl_4 in photochemical synthesis. Further studies are in progress in our laboratory.

Experimental Section

Apparatus. ^1H NMR spectra have been measured with a Bruker WH-90 spectrometer operating at 90-MHz. Chemical shift values are given in the δ scale with respect to Me_4Si as an internal standard. Infrared spectra were recorded on a Perkin-Elmer 710B infrared spectrophotometer and mass spectra were taken with a AE1 MS902 mass spectrometer.

Materials. Carbazole was an Eastman Organic Chemical and was used without any further purifications. Carbon tetrachloride from American Chemicals was spectrograde quality and it was washed with a saturated sodium carbonate solution and then repeatedly with water, dried with calcium chloride and P_2O_5, and redistilled. 3-Methylpentane (3-MP), pure grade (99%), was obtained from Phillips Petroleum Co. and was further purified along with ethanol by refluxing with concentrated sulfuric acid (4 mL of H_2SO_4/1000 mL of solvent) for 24 h. The acid was removed by washing with distilled water and the solvent was dried over P_2O_5 or sodium and was distilled twice before use.

General Procedure. Carbazole solutions (0.005 M) in pure CCl_4 or 0.1 M CCl_4 in ethanol or 3-MP were deoxygenated with oxygen-free argon and irradiated in a Pyrex Hanovia immersion-well reactor for 1 h with a Hanovia 679A36, 450-W medium-pressure mercury lamp. Hydrogen chloride generated during these reactions was neutralized with sodium carbonate. The precipitated sodium bicarbonate and excess sodium carbonate were removed from the solutions by filitration. The filtrates were concentrated. Irradiation of carbazole solutions (0.005 M, 1 h) in CCl_4 was also carried out in the presence of NH_3. During the irradiation ammonia gas was bubbled through the solution. Hydrogen chloride generated during the photochemical reaction was thus removed from the reaction medium. After irradiation, precipitated NH_4Cl was filtered and the filtrate was concentrated.

The photochemical products were then analyzed by TLC, detected by UV (using Eastman-Kodak TLC plates, silica gel 13181), and separated by column chromatography. The columns were packed with silica gel (Kieselgel 60, Merck, particle size 0.040–0.063 mm). Developing systems consisted of petroleum ether (low-boiling fraction) and ethyl ether or benzene and ethanol.

Spectral Characteristics of Products. 1-(Carboethoxy)carbazole (1) (ethyl 1-carbazolecarboxylate): white crystals (R_f 0.65, petroleum ether–ethyl ether 3:1); ^1H NMR ($CDCl_3$) δ 1.47 (t, J = 7 Hz, 3 H, methyl), 4.49 (q, J = 7 Hz, 2 H, methylene), 7.16–7.52 (m, 3 H, arom), 8.05, 8.14, 8.22, 8.31 (2 d, 4 H, arom); IR (Nujol film) $\bar{\nu}_{max}$ 3370 (s, NH), 1665 (vs, C=O), 1590 (s), 1480 (s), 1300 (m), 1290 (s), 1250 (vs), 1210 (vs), 1195 (s), 1170 (s), 1130 (vs), 1050 (m), 1040 (m), 1005 (m), 995 (m), 740 (s), 710 (s) cm^{-1}; mass spectrum (70 eV) (mol wt for $C_{15}H_{13}NO_2$ 239.28), m/e 239 (M^+, 45.0), 194 (24.2), 193 (100), 166 (45.1), 165 (58.6), 164 (37.0), 140 (16.1), 139 (44.6), 138 (15.9).

3-(Carboethoxy)carbazole (2) (ethyl 3-carbazolecarboxylate): white crystals (R_f 0.17, petroleum ether–ethyl ether, 3:1); ^1H NMR ($CDCl_3$) δ 1.45 (t, J = 7 Hz, 3 H, methyl), 4.45 (q,

J = 7 Hz, 2 H, methylene), 7.28–7.48 (m, 3 H, arom), 8.09–8.20 (m, 3 H, arom), 8.83 (s, 1 H, arom); IR (Nujol film) $\bar{\nu}_{max}$ 3270 (s, NH), 1680 (vs, C=O), 1615 (m), 1590 (s), 1325 (s), 1280 (s), 1265 (vs), 1255 (vs), 1235 (s, 1220 (m), 1120 (m), 1090 (s), 1020 (m), 900 (m), 760 (m), 745 (m), 735 (m), 715 (s) cm^{-1}; mass spectrum (70 eV) (mol wt for $C_{15}H_{13}NO_2$ 239.28), m/e 239 (M^+ 70.2), 195 (15.8), 194 (100), 193 (4.2), 166 (37.9), 165 (6.8), 164 (6.4), 139 (22.1).

***N*-(Trichloroethylene)carbazole (3)**: single crystals (R_f 0.81, petroleum ether–ethyl ether, 100:1); ^1H NMR ($CDCl_3$) δ 7.28–7.63 (m, 6 H, arom), 8.02–8.13 (m, 2 H, arom); IR (film) $\bar{\nu}_{max}$ 1590 (w), 1460 (w), 1430 (vs), 1410 (w), 1320 (vs), 1290 (m), 1210 (m), 1140 (s), 955 (m), 825 (s), 760 (s), 740 (vs), 705 (s) cm^{-1}; mass spectrum (70 eV) (mol wt for $C_{14}H_8NCl_3$ 296.58), m/e 301 (M^+, 3.3), 299 (M^+, 31.9), 297 (M^+, 94.5), 295 (M^+, 97.3), 264 (5.8), 262 (30.3), 260 (54.0), 227 (33.4), 225 (100), 190 (27.5), 178 (3.5), 166 (4.3).

***N*,*N*'-Dicarbazyl (4)**: white crystals (R_f 0.67, petroleum ether–ethyl ether, 100:1); ^1H NMR ($CDCl_3$) δ 6.77–6.91 (m, 4 H, arom), 7.21–7.40 (m, 8 H, arom), 8.08–8.26 (m, 4 H, arom); IR (film) $\bar{\nu}_{max}$ 1610 (m), 1595 (m), 1570 (w), 1475 (m), 1445 (s), 1435 (s), 1325 (s), 1305 (s), 1265 (m), 1225 (vs), 1140 (w), 1015 (w), 1000 (w), 990 (w), 920 (w), 740 (vs), 710 (s) cm^{-1}; mass spectrum (70 eV) (mol wt for $C_{24}H_{16}N_2$ 332.41), m/e 332 (M^+, 52.1), 166 (100).

***N*-Cyanocarbazole (5)**: white crystals (R_f 0.64, petroleum ether–ethyl ether, 10:1); ^1H NMR ($CDCl_3$) δ 7.32–7.73 (m, 6 H, arom), 7.95–8.10 (m, 2 H, arom); IR (film) $\bar{\nu}_{max}$ 2220 (vs, C≡N), 1610 (vw), 1595 (m), 1580 (vw), 1480 (w), 1470 (m), 1440 (vs), 1420 (m), 1340 (vs), 1300 (m), 1220 (s), 1150 (vs), 1130 (w), 1015 w), 925 (m), 850 (m), 750 (vs), 710 (s) cm^{-1}; mass spectrum (70 eV) (mol wt for $C_{13}H_8N_2$ 192.22), m/e 192 (M^+, 100), 166 (7.4), 165 (13.6), 164 (12.8).

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Restricted Rotation in Pentaarylpyrroles

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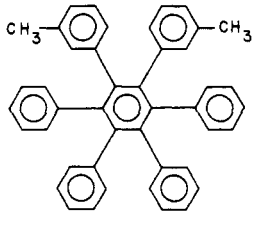
It is well-known that hexaarylbenzenes, pentaarylbenzenes, and analogous molecules exist in conformations wherein the peripheral aryl rings are approximately perpendicular to the plane of the central ring on the NMR time scale.[1-4] Properly substituted molecules such as 1



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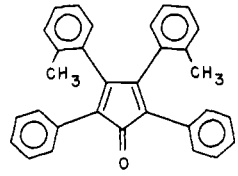

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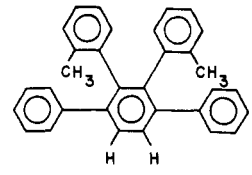
display rotational isomerism resulting from restricted rotation about the single bonds joining the central and peripheral rings. Previously reported free energies of activation for stereoisomerization in these compounds range from ~15 to 38 kcal/mol. Several of the factors which influence the magnitude of these rotational barriers have been investigated. The steric requirement of substituents in the ortho positions of the rotating rings has been found to be important,[1,2] as has the steric bulk of a substituent at *any* position on the central ring.[2-4]

Qualitatively, one would expect that decreasing the size of the central ring (e.g., to a five-membered ring) might lower the energy barrier to rotation of the peripheral rings. However, a quantitative determination of the magnitude of the barrier-lowering stereoisomerization in these systems has been lacking. The work described below provides such a determination.

The best indication to date of the influence of central ring size on rotational barriers in polyaryl systems comes from the work of Haywood-Farmer and Battiste.[5] These workers found that the free energy of activation for stereoisomerization of tetraarylcyclopentadienone 2 by rotation



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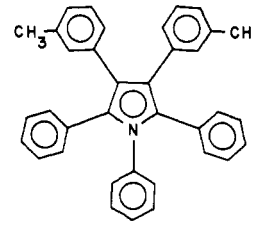

4

of the *o*-tolyl rings was $\Delta G^{\ddagger}$ = 21.8 kcal/mol. The corresponding barrier in tetraarylbenzene 3 was >25.6 kcal/mol. The difference of 3.8 kcal/mol is clearly not a very useful indication of the effects of ring size. Only a lower limit was obtained for the free energy of activation in 3. In addition, 2 and 3 both feature substituents other than aryl groups on the central ring. As mentioned above, such substituents can exert substantial steric influence through buttressing effects even though they may be remote from the site of aryl rotation.[2-4] Finally, the central ring of 3 is aromatic, whereas that of 2 is not. This difference might affect the ease of deformation of this ring in the transition state for rotation. As pointed out by Haywood-Farmer and Battiste, additional work in this area is needed.

A more satisfactory model system for evaluating the effect of ring size might be hexaarylbenzene 1 and an analogous compound having a five-membered central ring. Hexaarylbenzene 1 would be particularly well suited for such a study because it has previously been shown[1,2] to exist in two diastereomeric forms at 0 °C on the NMR time scale (an achiral conformer with both methyl groups on the same side of the plane of the central ring and a *dl* pair with the methyl groups on opposite sides). When a sample of 1 was warmed in the NMR spectrometer, the two methyl group resonances arising from these two diastereomers coalesced to a singlet as stereoisomerization became rapid ($\Delta G^{\ddagger}_{294}$ = 17.0 kcal/mol by NMR line-shaped analysis).[2] Although one might envision the preparation of a suitable pentaarylcyclopentadienyl radical or anion for comparison with 1, pentaarylpyrrole 4 provides a more easily accessible model which is not complicated by the presence of an unpaired electron or a negative charge and associated cation. This pyrrole was prepared by refluxing nitrosobenzene and the appropriate tetraarylcyclopentadienone in pyridine (see Experimental Section).

By analogy with hexaarylbenzenes[1] and biaryls, pentaarylpyrroles are expected to exist either in a perpendicular conformation with the five peripheral rings approximately at right angles to the plane of the central ring or in a propeller-like conformation with a low barrier to interconversion of propeller forms via an idealized transition

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