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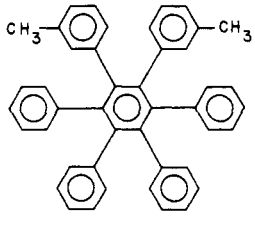
It is well-known that hexaarylbenzenes, pentaarylbenzenes, and analogous molecules exist in conformations wherein the peripheral aryl rings are approximately perpendicular to the plane of the central ring on the NMR time scale.[1-4] Properly substituted molecules such as 1



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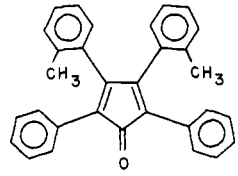

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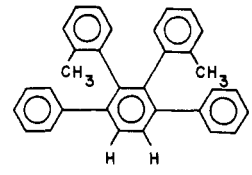
display rotational isomerism resulting from restricted rotation about the single bonds joining the central and peripheral rings. Previously reported free energies of activation for stereoisomerization in these compounds range from ~15 to 38 kcal/mol. Several of the factors which influence the magnitude 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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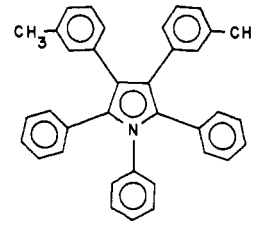

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of the *o*-tolyl rings was $\Delta G^{\ddagger}$ = 21.8 kcal/mol. The corresponding barrier in tetraarylbenzene 3 was >25.6 kcal/mol. The difference of 3.8 kcal/mol is clearly not a very useful indication of the effects of ring size. Only a lower limit 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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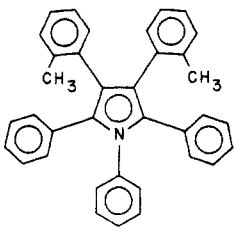
state with the perpendicular conformation. In either case, a pentaarylpyrrole would have an effective time-averaged perpendicular conformation on the NMR time scale. The NMR results described below are consistent with this expectation, and in the absence of more conclusive information, the stereochemistry of these compounds will be analyzed in terms of this framework.

In the limit of slow rotation, **4** would exist in diastereomeric forms similar to those observed for **1**, and two methyl resonances would be expected in the ^1H NMR spectrum. However, the 100-MHz ^1H NMR spectrum of **4** in $CDCl_3$ at 30 °C featured only a single sharp methyl resonance at 2.09 ppm. Cooling the sample did not cause this resonance to broaden. Only a single methyl resonance was observed even at −85 °C for a solution of **4** in 4:3 $CDCl_3/CS_2$.

There are three reasonable explanations for the failure to observe two methyl group resonances in the low-temperature NMR spectrum of **4**. Either rotation is slow but the two resonances are accidentally isochronous, or one diastereomer is thermodynamically much more stable than the other, or rotation is still rapid at −85 °C, and an averaged resonance is being observed. If the last explanation were correct, then increasing the steric bulk in the ortho positions of the rotating rings should raise the barrier and perhaps allow its measurement. In order to investigate this possibility, **5** was prepared by a route similar to that described for **4**.



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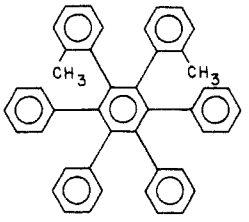

6

Indeed, at 50 °C the 100-MHz ^1H NMR spectrum of **5** in nitrobenzene-d_5 solution featured two sharp methyl resonances of essentially equal intensity separated by 10.2 Hz. This spectrum indicates that the two expected diastereomers are present in essentially equal amounts and that stereoisomerization is slow on the NMR time scale. When the sample was warmed, the two resonances coalesced to a singlet at ~101 °C which sharpened on further heating. A complete line-shape analysis of the data using spectra at eight temperatures yielded $\Delta G^{\ddagger}_{374} = 19.9$ kcal/mol for isomerization. By analogy with hexaarylbenzenes,[2] stereoisomerization presumably occurs via an uncorrelated rotation of an individual 2-methylphenyl ring through the plane of the central ring.

The barriers to stereoisomerization of the two diastereomers of hexaarylbenzene **6**, which also features ortho methyl groups on adjacent rings, were previously found to be 37.6 and 38.1 kcal/mol by classical kinetic methods.[1,2] Thus, the difference in free energies of activation between **5** and **6** is ~18 kcal/mol. Most of this difference may be ascribed to decreased steric repulsions in the transition state for **5**, relative to **6**, which are in turn a consequence of the larger angle between adjacent rings. Differences in bond lengths, ring deformability, etc. are necessarily also present, but these effects are undoubtedly of less importance.

The large effect of ring size found for **5** and **6** suggests that the failure to observe two resonances even in the low-temperature ^1H NMR spectrum of **4** was very likely due to rapid interconversion of diastereomers. The free energy of activation for stereoisomerization of **1** is ~21 kcal/mol lower than that for **6**. A decrease of roughly the same magnitude for **4** relative to **5** would suggest that the barrier for **4** would probably be too low to measure under the experimental conditions employed.

The large effect of ring size on rotational barriers in these systems also suggests that the free energy of activation for stereoisomerization of tetraarylbenzene **3** is significantly greater than 25.6 kcal/mol. This suggestion is in accord with previous findings in the hexa- and pentaarylbenzene systems.[1-3]

Finally, the relatively small difference in rotational barriers for **2** and **5** is undoubtedly not solely a result of steric differences between doubly bound oxygen and a phenyl group, because bond lengths, bond angles, and the ease of deforming the central ring may differ significantly in these two compounds. In general, one might expect steric buttressing effects of the type found to be important in hexa- and pentaarylbenzenes[3] to be much smaller in five-membered rings because, as shown here, steric effects in general are much smaller in these systems.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories. ^1H NMR spectra were obtained on a Varian XL-100 spectrometer and refer to ~20% solutions in chloroform-*d* with tetramethylsilane as an internal reference unless specified otherwise. For the dynamic NMR studies temperature measurements were calibrated by using an ethylene glycol standard and the temperature–shift correlations of Van Geet.[6] Line-shape analyses were performed as described previously.[2]

3,4-Bis(3-methylphenyl)-1,2,5-triphenylpyrrole (4) was prepared by using a method similar to that employed for pentaphenylpyrrole.[7] A solution of 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone[2,8] (1.1 g, 2.7 mmol) and nitrosobenzene (0.51 g, 7.2 mmol) in 10 mL of pyridine was refluxed for 72 h under a nitrogen atmosphere. The solvent was removed by distillation at reduced pressure, and the resulting solid was purified by crystallization and vacuum sublimation to yield the desired pyrrole: 0.040 g (3.6% yield); mp 217.5–218 °C. The ^1H NMR spectrum featured resonances at δ 2.09 (6 H, s, CH_3) and 6.66–7.19 (23 H, m, aromatic H). The mass spectrum yielded the expected molecular ion at *m/e* 475. Anal. Calcd for $C_{36}H_{29}N$: C, 90.91; H, 6.15; N, 2.95. Found: C, 90.81; H, 6.22; N, 2.93.

3,4-Bis(2-methylphenyl)-1,2,5-triphenylpyrrole (5) was prepared as described above for **4** from 3,4-bis(2-methylphenyl)-2,5-diphenylcyclopentadienone[5] (0.30 g, 0.73 mmol) and nitrosobenzene (0.20 g, 1.9 mmol). After vacuum sublimation, white crystals of **5** were obtained: 0.025 g (8% yield); mp 207–207.5 °C. The ^1H NMR spectrum was consistent with the proposed structure with resonances at δ 1.87 (3 H, s, CH_3), 1.91 (3 H, s, CH_3), and 6.69–7.19 (23 H, m, aromatic H). The mass spectrum yielded the expected molecular ion at *m/e* 475. Anal. Calcd for $C_{36}H_{29}N$: C, 90.91; H, 6.15; N, 2.95. Found: C, 90.75; H, 6.16; N, 2.93.

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Registry No. 2, 65375-82-8; **4**, 76466-79-0; **5**, 76466-80-3; 3,4-bis(3-methylphenyl)-2,5-diphenylcyclopentadienone, 64897-54-7; nitrosobenzene, 586-96-9.

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