# Internal Rotation in *peri*-Phenylnaphthalenes[1]

Roger L. Clough[2] and John D. Roberts*

*Contribution No. 5528, Gates and Crellin Laboratories of Chemistry,
California Institute of Technology, Pasadena, California 91125*

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A 180° rotation about a phenyl–naphthyl bond is expected to be effectively blocked for derivatives of the *peri*-diphenylnaphthalenes, in which steric requirements force the phenyl rings to assume a face-to-face conformation. However, surprisingly low rotational energy barriers have been found. The preparation and the measurement of the barrier to phenyl ring rotation of a derivative of the highly crowded 1,4,5,8-tetraphenylnaphthalene system is described. The barrier for this substance is 14.9 kcal/mol compared with 16.4 kcal/mol determined for 1,8-diphenyl-naphthalene; both of these barriers are much lower compared with the 33.5 kcal/mol reported for the stereotopically similar [3.4]paracyclophane. The differences are discussed in terms of a rotational transition state having large deformations of the naphthalene ring.

Molecular models suggest that the only possible geometry for 1,8-diphenylnaphthalene will have the phenyl rings face to face, **1**, and this has been confirmed by recent x-ray diffraction.[3] Even in this conformation there is severe crowding of the phenyl rings. As a result, the aryl rings would be ex-
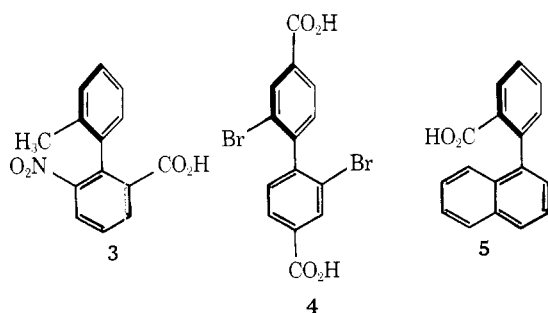

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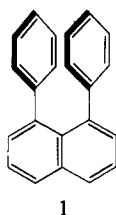
pected to have a high barrier to a 180° rotation about the aryl–naphthyl bond. Indeed, CPK space-filling models would seem to indicate that such a rotation is in fact impossible, except by breaking one or more bonds. House and co-workers have prepared several derivatives of 1,8-diphenylnaphthalene having a substituent at one meta position of each phenyl ring, with the expectation that they would be able to isolate cis and trans isomers.[4] However, it was not found possible to obtain separate isomers, and, instead, a single crystalline compound was isolated in each case. Subsequent NMR measurements[5] on the derivative, **2**, showed that the barrier to rotation was


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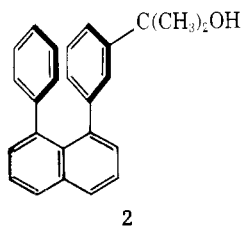
only 16.4 kcal/mol, consistent with rapid rotation at room temperature.

The 1,8-diarylnaphthalenes may be profitably compared with the ortho-substituted biphenyls, for which many examples having rotational barriers high enough to allow separation of optical isomers are known, for example, **3** and **4**.[6] The naphthyl derivative, **5**, has also been resolved,[7] as has α,α'-


binaphthyl, **6,** for which a rotational barrier of 22.5 kcal/mol was obtained.[8] Cram has reported that the [3.3]paracyclophane, **7,** showed no tendency to racemize at temperatures up to 240 °C[9] and that the [3.4]paracyclophane, **8,** racemized only


7   8
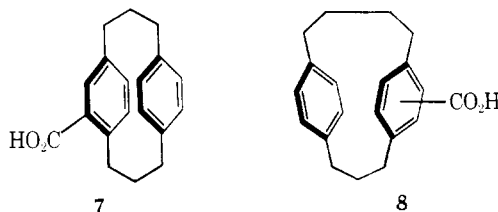
slowly at 160 °C.[10] The barrier to phenyl ring rotation in the latter was calculated to be 33.5 kcal/mol. These two compounds provide a striking contrast to derivatives of **1**, for which similar steric requirements would be inferred.

Several other naphthalene derivatives having different types of peri substituents have been recently reported to have what seem surprisingly low barriers to rotation about the naphthyl-substituent bond.[11,12] For example, the barrier to rotation of the *tert*-butyl group of **9** was <6 kcal/mol and that of **10** was estimated at about 6.5 kcal/mol.[11]


9   10
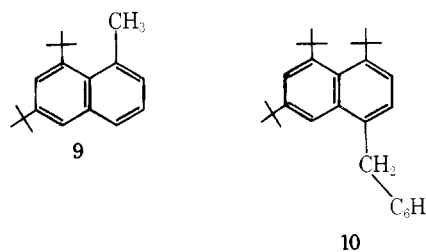
We report here the synthesis and measurement of the rotational barrier of the highly strained **11**, which has two sets of crowded *peri*-phenyl groups.

11
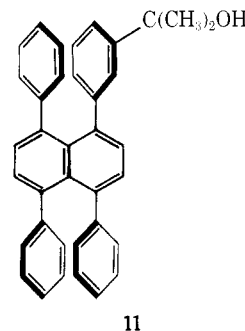
Synthesis and NMR Study of 11

The synthetic scheme for **11** had **12** as a key intermediate, with the *m*-chloro group intended to serve as a marker which

would be inert to conditions of the synthetic sequence, but which would permit direct functionalization of the aromatic ring after construction of the naphthalene framework. In-
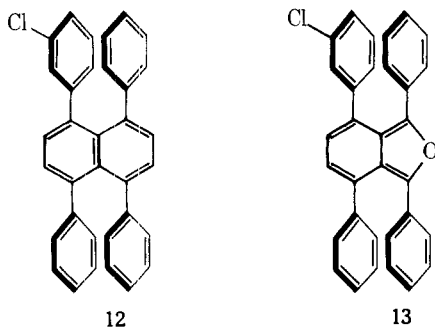
12   **13**

termediate **12** was synthesized in eight steps starting from *m*-chlorobenzaldehyde and involving preparation of the chlorotetraphenylbenzoisofuran, **13,** with subsequent Diels–Alder addition and aromatization, similar to the synthetic routes used previously in preparation of several substituted napththalenes including 1,4-diphenylnaphthalene,[13] 5,10-diphenylanthracene,[14] and 1,4,5,8-tetraphenylnaphthalene.[15]

The chloro group of **12** proved to be highly inert, and standard procedures for generating the anion failed. Stirring with a solution of *n*-butyllithium gave no halogen–metal exchange. No reaction could be induced between **12** and strips of lithium metal and no reaction was observed when **12** was added to a freshly prepared dispersion of sodium. However, when **12** was added to an excess of fine lithium dust (140 mesh) under argon with bromobenzene present to activate the metal with ether as a solvent, the solution turned to a deep purple on heating to reflux. Addition of the organolithium compound to acetone in ether gave **11** in 57% yield.

When ring rotation of **11** is slow on the NMR time scale, its methyl groups become diastereotopic. The methyl proton NMR resonances of **11** at 100 °C were a single sharp peak, which, on lowering the temperature, broadened and at 5 °C began to separate into two equal signals. Visual matching using computer-generated spectra allowed calculation of the energy barrier for rotation, $\Delta G^{\ddagger}$, of 14.9 kcal/mol.[16]

The Rotational Mechanism of *peri*-Phenylnaphthalenes

Detailed calculations on the rotational barriers of some 2,2′-substituted biphenyls have been reported by Westheimer,[17] who showed that the rotational intermediates must have geometric deformations local to the interannular bond. Important distortions include bending of the ortho substituents away from each other, interannular bond stretching, and C–H (ortho) bond compression.

For *peri*-phenylnaphthalenes, a rotational transition state may be visualized in which one phenyl ring must turn to a position perpendicular to the adjacent *peri*-phenyl ring.[18] There are two modes of distortion available to the intermediate which we believe responsible for the low barriers observed. These two modes, which have no analogue in the biphenyls, are in-plane and out-of-plane splaying of the peri groups. In-plane splaying can occur both by a bending of the exocyclic naphthyl-substituent bond which increases the C9–C1-substituent angle and by an opening of the C1–C9–C8


angle of the naphthalene nucleus. C1–C9–C8 angle opening can be especially effective, because the distance between the peri substituents is increased without a concomitant increase in crowding between the substituent and the adjacent naphthyl proton. Out-of-plane splaying would involve displacement of the peri substituents (and to a lesser extent, the naphthalene atoms C1 and C8) to opposite sides of the naphthalene plane.

Recent x-ray investigations[19] demonstrate a surprising lack of rigidity of the naphthalene ring and show that nonbonded interactions between bulky peri substituents are considerably relieved by large in-plane and out-of-plane distortions of the type described above. The strain energy is effectively absorbed by the naphthalene nucleus; this is accomplished by a distribution of the strain throughout the framework which includes angle bending, bond stretching and compression, and in- and out-of-plane nuclear displacements. Distortions are substantial.[20-22] In 1,8-diphenylnaphthalene[3,22] the C1–C9–C8 angle is forced open to over 126°, the C9–C1-phenyl angles open to more than 125°, and the naphthyl–phenyl out-of-plane angles are about 2°. Such distortions can become even larger. For example, in the related *peri*-diphenylacenaphthene, due to a pinching effect at the 4,5 carbon atoms, the C1–C9–C8 angle is 129.4°.[23] For the extremely crowded 1,8-diiodonaphthalene, the C1–C9–C8 angle exceeds 130°.[24]

These x-ray determined structures provide insight into the geometry of the rotational transition state of the 1,8-diarylnaphthalenes, although to achieve the more highly strained geometry of the rotational intermediate, the distortions must be considerably enhanced. Because of the considerable flexibility of the naphthalene nucleus, the dramatic lowering of the rotational barriers of both 1,8-diphenylnaphthalene and 1,4,5,8-tetraphenylnaphthalene as compared with [3.3]paracyclophane and [3.4]paracyclophane becomes understandable. The reason is that the cyclophanes lack the possibility of phenyl–phenyl splaying. The low barriers of peri-substituted naphthalenes compared with systems **3, 4, 5,** and **6** are also understandable because in peri-substituted naphthalenes the ground-state strain is sufficiently large to allow the transition state for rotation to be achieved more readily than for simple ortho-substituted biphenyl derivatives, where ground-state interactions are small.

The difference between the rotational barriers in 1,8-diphenylnaphthalene and 1,4,5,8-tetraphenylnaphthalene derivatives is also seen as a consequence of the involvement of the naphthalene ring distortions in the phenyl ring rotation. The tetraphenyl compound has crowding interactions at both pairs of peri positions, making this molecule more strained than the 1,8-diphenylnaphthalene. The increased strain enhances the distortion of the naphthalene nucleus and consequently facilitates attainment of the rotational transition-state geometry. Evidence of this synergistic distortion is shown by the ground-state geometries of these two molecules, as determined by x-ray diffraction.[22] The distribution of the distortion is somewhat different in these molecules,[22] but the tetraphenyl compound has the larger overall phenyl–phenyl splaying as shown by the ground-state dihedral angle between the two phenyl rings in 1,8-diphenylnaphthalene of 20° and that in 1,4,5,8-tetraphenylnaphthalene of about 36°.

A further example consistent with conjoint peri distortion and ring rotation is provided by the comparison of the ease of racemization of the binaphthyl derivatives, 8,8′-dicarboxy-1,1′-binaphthyl, **20,** and 2,2′-dicarboxy-1,1′-binaphthyl, **21.** A cursory inspection of the structural formulas, **20** and **21,** might lead one to expect rather similar restrictions to a 180° rotation about the naphthyl–naphthyl bond. In fact, resolved **21** shows no change in optical activity after 8 h at 175 °C,[25a] while **20** has a half-life with respect to racemization of only
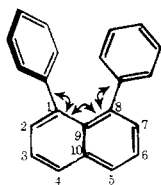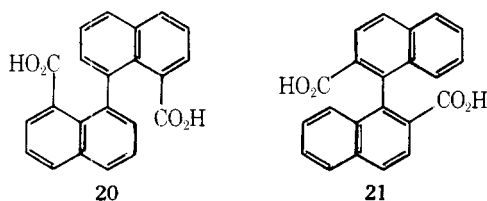
about 15 min at 50 °C (roughly comparable to α,α'-binaphthyl itself).[25b] However, the ground-state peri crowding in **20** is highly conducive to the naphthalene splaying interaction necessary for rotation. The low rotational barriers in other peri-substituted naphthalene derivatives, such as **9** and **10**, can be accounted for in the same way.[11]

Experimental Section

Triphenylcinnamylphosphonium Chloride, 14. Triphenylcinnamylphosphonium chloride was prepared by the method of Organic Syntheses.[26] From 40 g (0.26 mol) of (3-chloropropenyl)benzene and 92 g (0.35 mol) of triphenylphosphine was obtained 101 g (93%) of **14** (mp 224–226 °C (lit.[27] mp 224–226 °C)) which was used without further purification.

1-(3-Chlorophenyl)-4-phenyl-1,3-butadiene, 15. The procedure from Organic Syntheses[26] for 1,4-diphenyl-1,3-butadiene was slightly modified for making the chlorinated derivative. Thus, 630 mL of 0.2 M lithium ethoxide (prepared from the dissolution of 2.1 g of lithium wire in 1.5 L of absolute ethanol) was added with stirring to a solution of 50 g (0.121 mol) of **14** and 18.04 g (0.127 mol) of *m*-chlorobenzaldehyde in 150 mL of absolute ethanol. A deep red-orange color developed, which faded after the mixture had been stirred at room temperature for 45 min. Addition of 600 mL of H_2O caused formation of precipitate, which was collected and washed with 150 mL of 60% aqueous ethanol. The crude diene was stirred with a solution of ethanol (20 mL) and refiltered to give 21 g (0.087 mol, 69%) of glossy, pale-yellow plates, which melted at 109–110 °C after recrystallization from ethanol–isopropyl alcohol and from cyclohexane: NMR δ (CDCl$_3$) 6.2–7.5 (m); IR (Nujol) 1009, 1092, 770 cm^{-1}; mass spectra Calcd for C$_{16}$H$_{13}$Cl 240.0706, 240.0706. Anal. Calcd for C$_{16}$H$_{13}$Cl: C, 79.83; H, 5.44: Cl, 14.73. Found: C, 79.60; H, 5.56; Cl, 14.46.

1,2-Dibenzoyl-3-(3-chlorophenyl)-6-phenylcyclohex-4-ene, 16. When the Diels–Alder reaction of **15** with *trans*-dibenzoylethylene was carried out in gently refluxing isopropyl alcohol for 8 h, only a brown oil resulted; however, the product could be prepared in reasonable yield under more vigorous conditions. Thus, 18 g (0.075 mol) of **15** and 20 g (0.08 mol) of *trans*-dibenzoylethylene were refluxed vigorously (no stirring; bath temperature = 136 °C) in 300 mL of isopropyl alcohol for 18 h. The mixture was allowed to cool to 50 °C and when the walls of the vessel were scratched with a glass stirring rod a white solid precipitated. The solid was removed by filtration at 50 °C, rinsed twice with 30 mL of warm isopropyl alcohol, then dissolved in acetone (1.5 mL/1 g) and filtered, and the filtrate was evaporated slowly to dryness yielding 15.5 g of **16** (0.033 mol, 44%). The infrared spectrum showed the presence of two carbonyl peaks, a major peak, at 1680 cm^{-1}, and a minor peak, at 1697 cm^{-1}, both different from the starting material peak (1600 cm^{-1}). Repeated recrystallizations failed to yield a sharply melting material. When the reaction was carried out with 24 h of reflux, the product showed almost exclusively the 1680-cm^{-1} peak. Recrystallization from isopropyl alcohol–acetone gave a white, crystalline solid (mp 136.5–139.5 °C); mass spectra Calcd for C$_{32}$H$_{25}$ClO$_2$ 476.1542, 476.1543. Aromatization of either the product with the two carbonyl peaks (presumably a mixture of isomers) or that with the single peak, by the method described below, gave similar good yields of compounds having identical spectra.

1,2-Dibenzoyl-3-(3-chlorophenyl)-6-phenylbenzene, 17. To a solution of 20.3 g (0.043 mol) of **16** in 130 mL of chloroform stirred under reflux was added dropwise (15 min) a solution of 90 mL of chloroform containing 4.3 mL of bromine. As the refluxing continued, large amounts of HBr were evolved. When the gas evolution had ceased (~30 min), the solvent was removed with a rotary evaporator to give a yellow-brown gummy substance which was crystallized by stirring overnight with absolute ethanol. Further purification was effected by stirring the finely powdered solid with 20 mL of methanol for 20 min and washing with 5 mL of methanol to yield 18 g (0.038 mol, 89%) of a white, crystalline solid which was recrystallized from isopropyl alcohol–acetone to give opaque rods: mp 150–153 °C; IR (Nujol) 1670 cm^{-1}; mass spectra Calcd for C$_{32}$H$_{21}$ClO$_2$, 472.1231, 472.1230.

4-(3-Chlorophenyl)-1,3,7-triphenylisobenzofuran, 13. Zinc dust (7 g), activated by stirring with dilute NaOH solution, then washed with water and ethanol, was added with stirring to a refluxing solution of 7.5 g (15.9 mmol) of **17** and 7 g of NaOH in 165 mL of ethanol. Refluxing for short reaction times was found to give only partial conversion. During 6 h of reflux, the solution turned bright yellow-green and then faded. The reaction mixture was filtered into 150 mL of glacial acetic acid, and 20 mL of water was added to the filtrate. The solution was evaporated to about 25 mL, and the heterogeneous aqueous mixture was extracted twice with benzene. The combined organic portions were filtered through 15 g of anhydrous sodium sulfate, evaporated to a syrupy yellow liquid, and left standing overnight to yield 6.5 g (14.2 mmol, 89%) of a brilliant-yellow solid having a powerful green fluorescence in benzene: mp 174.5–177 °C; IR (Nujol) 1470, 855 cm^{-1} (no carbonyl); mass spectra Calcd. for C$_{32}$H$_{21}$ClO 456.1282, 456.1281. Anal. Calcd for C$_{32}$H$_{21}$ClO: C, 84.11; H, 4.63; Cl, 7.76. Found: C, 84.23; H, 4.92; Cl, 7.80.

Adduct of 13 with Acrolein, 18. Freshly distilled acrolein (5 mL) was added to a stirring, gently refluxing solution of 6.5 g (14.2 mmol) of **13** in 50 mL of benzene. After 30 min, an additional 2 mL of acrolein was added. Twenty minutes later, the bright yellow had faded to give a nearly colorless solution, and the reaction was stopped. The crude mixture was evaporated to dryness and crystallized from 10 mL of isopropyl alcohol to give a white product (6 g, 11.7 mmol, 83%): mp 148–151 °C; IR (Nujol) 1725 cm^{-1} (carbonyl); NMR δ (CDCl$_3$) 9.3 (m, 1), 3.4 (m, 1), 2.5 (m, 2), 6.6–6–7.6 (m, 21); mass spectra showed only peaks due to the retro-Diels–Alder product, **13**. Anal. Calcd for C$_{35}$H$_{25}$O$_2$Cl: C 81.94, H 4.91, Cl 6.91. Found: C 82.11, H 4.68, Cl 6.86.

5-(3-Chlorophenyl)-1,4,8-triphenyl-2-naphthaldehyde, 19. Anhydrous, gaseous HCl was bubbled for 25 min through a stirred solution of 7 g (13.7 mmol) of **18** in 50 mL of glacial acetic acid at 0 °C. The starting material largely dissolved, yielding a reddish solution. The reaction mixture was stirred for an additional hour without cooling after the addition of the HCl was stopped. The chilled mixture was filtered and the filtrate was rinsed with 8 mL of cold acetic acid. The crude yellow product (5 g, 10.1 mmol, 74%) was contaminated with **13**. Stirring with a small amount of isopropyl alcohol removed most of this impurity. Recrystallization from isopropyl alcohol gave light-yellow crystals of **19**: mp 208–210 °C; IR (Nujol) 1683 cm^{-1} (aromatic aldehyde); mass spectra Calcd for C$_{35}$H$_{23}$ClO 494.1437, 194.1437.

1-(3-Chlorophenyl)-4,5,8-triphenylnaphthalene, 12. The attempted decarbonylation of **19** with tris(triphenylphosphine)rhodium(I) chloride in refluxing benzene resulted only in precipitation of the red dimer of the rhodium complex, a result which has been observed before with other sterically crowded aldehydes.[28] Nitriles are reported to stabilize the monomeric rhodium species.[28] When 1 g of **19** was heated at 160–165 °C in 9 mL of benzaldehyde, the reaction was judged complete by TLC analysis after 8 min. Chromatography of the crude mixture on silica gel with hexane as the eluent afforded **12** (0.80 g, 80%). Recrystallization from hexane gave clear prisms: mp 216–217 °C; NMR δ (CDCl$_3$) 7.5 (broad singlet, 4), 7.0 (broad singlet 19); mass spectra Calcd for C$_{34}$H$_{23}$Cl 466.1490, 466.1488.

Preparation of Carbinol 11. All equipment was dried immediately before use in an oven at 150 °C overnight. The reagents were transferred to the reaction vessel in a drybox under argon. A positive pressure of argon was maintained in the reaction vessel throughout the course of the reaction. A solution of 0.23 g (0.5 mmol) of **12** in 5 mL of ether was combined with 0.04 g of lithium dust (Alfa Chemical Co., 140 mesh) and 2 drops of bromobenzene. The solution was refluxed with stirring for 20 min; a deep purple color was observed 2 min after the start of refluxing. The mixture was added to a solution of 1 mL of anhydrous acetone in 10 mL of ether and, after 5 min, was hydrolyzed. Two successive preparative TLC runs using 15% ether in benzene (R_f 0.45) gave 0.14 g (57%) of **11** as clear oil: IR (Nujol) 3590 cm^{-1} (O–H stretch); NMR δ (CDCl$_3$) 7.46 (s, 4), 6.85–7.15 (s, 19), 1.48 (s, 6), 1.90 (broad s, 1); ^{13}C NMR (in ppm relative to Me$_4$Si, in CDCl$_3$) 31.4 (methyl), 81.0 (hydroxyl carbon); mass spectra Calcd for C$_{37}$H$_{30}$O 490.2293, 490.22965.

Rotational Barrier Measurements. The proton spectra for the rotational-barrier measurement of **11** were obtained over a temperature range of 70 to −30 °C using a Varian Associates HR-220 NMR spectrometer. The temperature was determined for each measurement from the peak separations of standard samples of either methanol or ethylene glycol. The methyl signal from **11** broadened steadily from a sharp singlet at the high-temperature limit to the coalescence point at 5 °C. The peak separation reached a maximum of 3.6 Hz at −10 °C. The natural line width of the methyl peak was taken to vary linearly from 1.1 to 1.5 Hz over the temperature range examined.

Computer-simulated line shapes were obtained with the program CLATUX[29] and were visually matched to the experimental spectra. From the pre-exchange lifetimes, the free energy of rotation was calculated for each measurement using the equation $\Delta G^{\ddagger} = 4.575T (10.32 + \log T - \log K_r)$. Good agreement was obtained, particularly for measurements made in the coalescence region. From the values between -11 and $+38$ °C, a $\Delta G^{\ddagger}$ of 14.9 ± 0.2 kcal/mol was obtained.

References and Notes

(1) Supported by the National Science Foundation.
(2) NDEA Title IV Fellow, 1971–1974.
(3) R. A. Ogilvie, Ph.D. Thesis, Massachusetts Institute of Technology, 1971.
(4) (a) H. O. House and R. W. Bashe II, *J. Org. Chem.*, **40**, 2942 (1965); **32**, 784 (1967); (b) H. O. House, R. W. Magin, and H. W. Thompson, *ibid.*, **28**, 2403 (1963).
(5) H. O. House, W. J. Campbell, and M. Gall, *J. Org. Chem.*, **35**, 1815 (1970).
(6) E. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, pp 156–162.
(7) D. M. Hall, S. Ridgwell, and E. E. Turner, *J. Chem. Soc.*, 2498 (1954).
(8) W. Theilacker and R. Hopp, *Chem. Ber.*, **92**, 2293 (1959).
(9) D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **4**, 204 (1971).
(10) H. J. Reich and D. J. Cram, *J. Am. Chem. Soc.*, **91**, 3517 (1969).
(11) J. E. Anderson, R. Franck, and W. Mandella, *J. Am. Chem. Soc.*, **94**, 4608 (1972).
(12) D. Fields and T. Regan, *J. Org. Chem.*, **36**, 2986 (1971).
(13) A. Etienne, A. Spire, and E. Toromanoff, *Bull. Soc. Chim. Fr.*, 750 (1952).
(14) G. Wittig, E. Knauss, and K. Niethammer, *Justus Liebigs Ann. Chem.*, **630**, 10 (1960).
(15) E. D. Bergmann, Sh. Blumberg, P. Bracha, and Sh. Epstein, *Tetrahedron*,

20, 195 (1964).
(16) In the absence of phenyl ring rotation, derivatives of 1,4,5,8-tetraphenylnaphthalene having a substituent in the meta position of one phenyl ring must exist as enantiomers. Whether or not ring rotation is rapid in solution, the possibility existed that the enantiomers could crystallize separately, as has been observed for other large dissymmetric aromatics including heptahelicene. Microscopic examination of crystals of **12** grown by slow evaporation of a hexane solution revealed that they are triclinic but have a center of symmetry and belong to the pinacoidal class, indicating that **12** crystallizes as a racemic mixture.
(17) (a) F. H. Westheimer and J. E. Mayer, *J. Chem. Phys.*, **14**, 733 (1946); (b) R. Reiger and F. H. Westheimer, *J. Am. Chem. Soc.*, **72**, 19 (1950); (c) F. H. Westheimer, "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956, Chapter 12.
(18) One recent result (R. L. Clough and J. D. Roberts, *J. Am. Chem. Soc.*, **98**, 1018 (1976)), readily understood with the model of phenyl ring rotation through an intermediate having this geometry, is the rotational barrier of 1,8-di-*o*-tolylnaphthalene which is 8 kcal/mol higher than that measured for **2**. The magnitude of the barrier is such that the postulated stable cis and trans isomers are capable of isolation. The increased barrier with 1,8-di-*o*-tolylnaphthalene is the result of unfavorable interactions of the *o*-methyl groups with the naphthyl C2 hydrogen atom in the rotational transition state.
(19) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).
(20) H. Einspahr, J.-B. Robert, R. E. Marsh, and J. D. Roberts, *Acta Crystallogr., Sect. B*, **29**, 1611 (1973).
(21) J.-B. Robert, J. S. Sherfinski, R. E. Marsh, and J. D. Roberts, *J. Org. Chem.*, **39**, 1152 (1974).
(22) R. L. Clough, W. J. Kung, R. E. Marsh, and J. D. Roberts, *J. Org. Chem.*, **41**, 3603 (1976).
(23) A detailed discussion of the cooperative influences of strain interactions at the two sets of peri positions on the geometry of the naphthalene nucleus is presented in ref 22.
(24) J. S. Sherfinski, J. D. Roberts, and R. E. Marsh, to be published.
(25) (a) V. Balasubramaniyan, *Chem. Rev.*, **66**, 585 (1966), and numerous references therein; (b) F. Bell and W. H. D. Morgan, *J. Chem. Soc.*, 1716 (1954); (c) M. Harris and C. Ling, *Chem. Ind. (London)*, 1378 (1962).
(26) *Org. Synth.*, **40**, 36 (1960).
(27) T. W. Campbell and R. N. McDonald, *J. Org. Chem.*, **24**, 1969 (1959).
(28) J. Tsuji and K. Ohno, *Synthesis*, **12**, 164 (1969).
(29) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

Centrosymmetric 1,5-Naphthyridine Derivatives: Synthesis, Tautomerism, and Thermal Rearrangements[1]

S. B. Brown[2] and M. J. S. Dewar*

*Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712*

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Efficient syntheses of the centrosymmetric 1,5-napthyridine derivatives 2–8 are reported. The 8-methoxy-1,5-naphthyridine 14 has been shown to undergo thermal rearrangement to its *N*-methyl isomer and thermal disproportionation to *N,N*-dimethyl and normethyl compounds. Tautomerism in hydroxy-1,5-naphthyridines has been investigated by UV spectroscopy in aqueous solution. Under these conditions the compounds studied exist predominantly as the pyridone tautomers. A remarkable alkylation reaction of the naphthyridine ring has been observed in the course of Lander rearrangement of 8. It has been found that 8 via its rearranged isomer 4 gives the centrosymmetric ring-methylated compound 5 when heated in the solid state with methyl iodide.
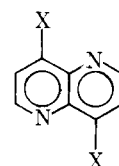
Introduction

In connection with our studies of organometallic coordination polymers that might prove useful as semiconductors,[3] we needed heteroaromatic compounds potentially capable of functioning as tetradentate ligands. We were particularly interested in obtaining tetradentate analogues of the well-known bidentate chelating agent 8-hydroxyquinoline (**1**). Such analogues could be derived on paper by incorporating two additional coordination sites across a center of symmetry in **1** or by substituting naphthyridine to form appropriate 4,8-disubstituted 1,5-naphthyridines. In the present work, we describe efficient syntheses of the centrosymmetric 1,5-naphthyridine derivatives **2–8**. Hydroxynaphthyridines throughout this work are shown schematically and named as their presumably more stable pyridone (i.e., keto) tautomers,

and evidence is presented that the latter tautomers indeed predominate in aqueous solution. Finally, we report novel results obtained during thermal rearrangement studies on alkoxynaphthyridines.
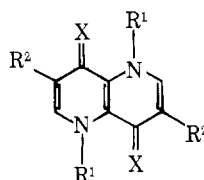
2, X = O; $R^1 = R^2 = H$
3, X = S; $R^1 = R^2 = H$
4, X = O; $R^1 = Me$; $R^2 = H$
5, X = O; $R^1 = H$; $R^2 = Me$

6, X = Cl
7, X = NH_2
8, X = OMe