

SYNTHESIS AND TRAPPING OF 3,4,3',4'-TETRADEHYDROBIPHENYL  
(BISBENZYNE)

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ABSTRACT

3,3'-Dicarboxy-4,4'-diaminobiphenyl was synthesized from *o*-nitrobenzoic acid following standard procedures. Diazotization of this compound with isoamyl nitrite, under aprotic condition gave diphenyl-4,4'-bis-diazonium-3,3'-dicarboxylate and subsequent thermal decomposition of this diazonium compound produced 3,4,3',4'-tetrahydrobiphenyl (bisbenzyne) as a reactive intermediate. Bisbenzyne was trapped with the diene 2,3,4,5,-tetraphenylcyclopentadienone via a [4+2] Diels-Alder cycloaddition reaction yielding the previously unreported 5,6,7,8,5',6',7',8', -octaphenyl-2,2'-binaphthyl. This novel compound was fully characterized by elemental analysis IR and <sup>1</sup>H NMR spectroscopy.

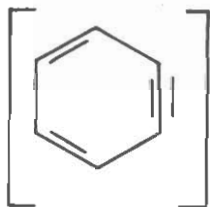
INTRODUCTION

Generally speaking organic chemical reactions can be divided up into either one-step reactions, e.g., SN2 dis-

placement; or multi-step processes. The latter reactions necessarily involve active intermediates such as free radicals, carbonium ions, carbocations,

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etc. An example among these active intermediates is benzyne(1).



(1)

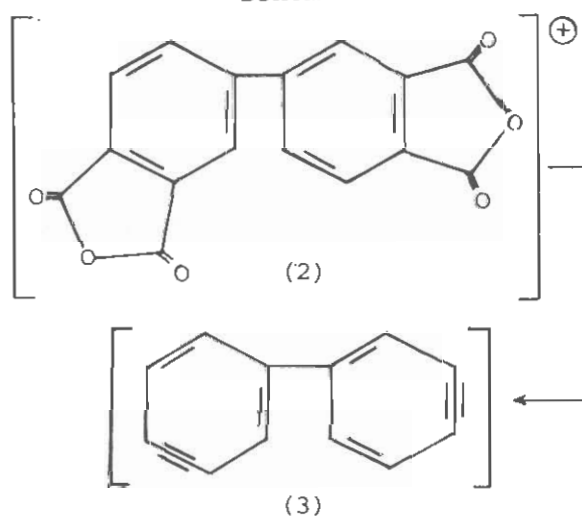
Benzyne, also referred to as 1,2-dehydrobenzene and 1,3-cyclohexa-5-yne is a short-life intermediate. Benzyne has been prepared by several methods. In almost all cases, benzyne is formed by a concerted or a stepwise elimination of two adjacent substituents in an aromatic ring, leaving the electrons distributed between two formerly bonding orbitals.

Benzyne can be generated from O-dihalobenzene [1,2], anthranilic acid [3,4], diphenyliodonium-2-carboxylate [5,6], O-aminophenylboronic acid [7], 2-azobenzoic acids [8-11], 2-carboxylbenzene diazonium chloride [12], 1,2,3-benzothiazole-1,1-dioxide [13], N-aminobenzotriazoles [14], and so on. Since benzyne is a reactive intermediate, it can not be isolated, but can be observed indirectly by using trapping species. Compounds often used as trapping agents are tetraphenylcyclopentadienone, anthracene, furan, cyclopentadiene, and diphenylisobenzofuran [5,6,15].

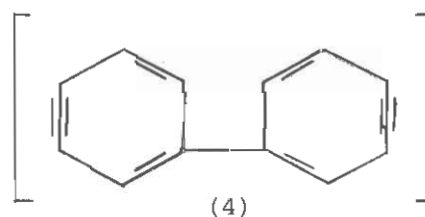
Although generation and trapping of benzyne has been widely studied,

little has been published on bisbenzyne. It has been reported that an ion of molecular weight 150, nominally bibenzyne (3) was formed by decomposition of 3,4,3',4'-biphenyltetracarboxylic anhydride (2) in mass spectrometer [16] (scheme 1). There is

scheme 1



no evidence in the literature of trapping of this bisbenzyne intermediate or of its formation in solution. A major goal of this research was to generate 3,4,3',4'-tetrahydrobiphenyl (4) in solution and to prove its existence indirectly by classical trapping experiments. A recent report on diaryne system has been published by H. Hart and et al [20,21]. A different diaryne system has also been reported by J. Nakayama, et al [22].



(4)

## RESULTS AND DISCUSSION

It is well established that anthranilic acid (5) is readily diazotized in solution by isoamyl nitrite under aprotic condition to yield benzenediazonium-2-carboxylate (6), and the subsequent thermal decomposition of (6) gives the benzyne intermediate (1), nitrogen, and carbon dioxide [15]. The presence of carbon dioxide can be detected with calcium hydroxide solution. The termination of reaction occurs when carbon dioxide is no longer evolved. The above technique to form benzyne avoids the isolation and handling of the hazardous and explosive benzenediazonium-2-carboxylate (6) and serves as a convenient preparative source of benzyne. The reaction can be effected by adding simultaneously a solution of the anthranilic acid (5) and a solution of isoamyl nitrite dropwise to a stirred, refluxing solution of benzyne ac-

ceptor. Gas evolution occurs immediately and ceases within a few minutes after the addition is complete. The above technique was used and benzyne generated was trapped by furan and tetraphenylcyclopentadienone (7) (scheme 2).

The adduct from furan and benzyne was verified by  $^1\text{H NMR}$  spectrum. The reaction of benzyne with compound (7) was carried out at  $85^\circ\text{C}$  and since the [4+2] adduct (8) is not stable at this temperature, it lost carbon monoxide and gave 1,2,3,4-tetraphenyl-naphthalene (9), in a 91% yield, which served as a model compound. It is interesting to point out that the dark purple tetraphenylcyclopentadienone (7) is a particularly favorable diene for experimentation because the adduct is colorless, so termination of the reaction can be followed by the discharge of the intense purple color.

Compound (9) was characterized by  $^1\text{H NMR}$  (Fig. 1), and IR spectroscopy.

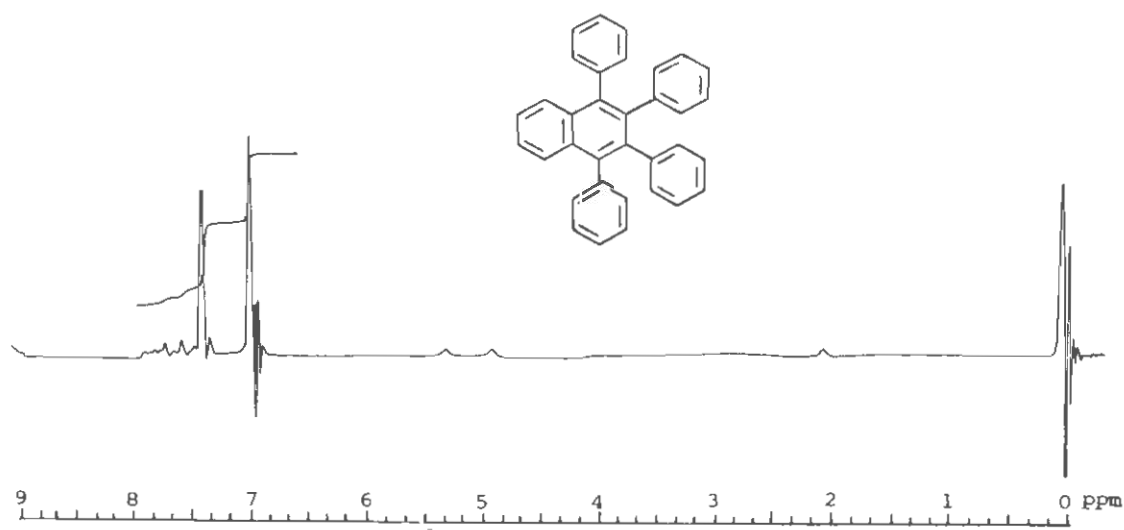
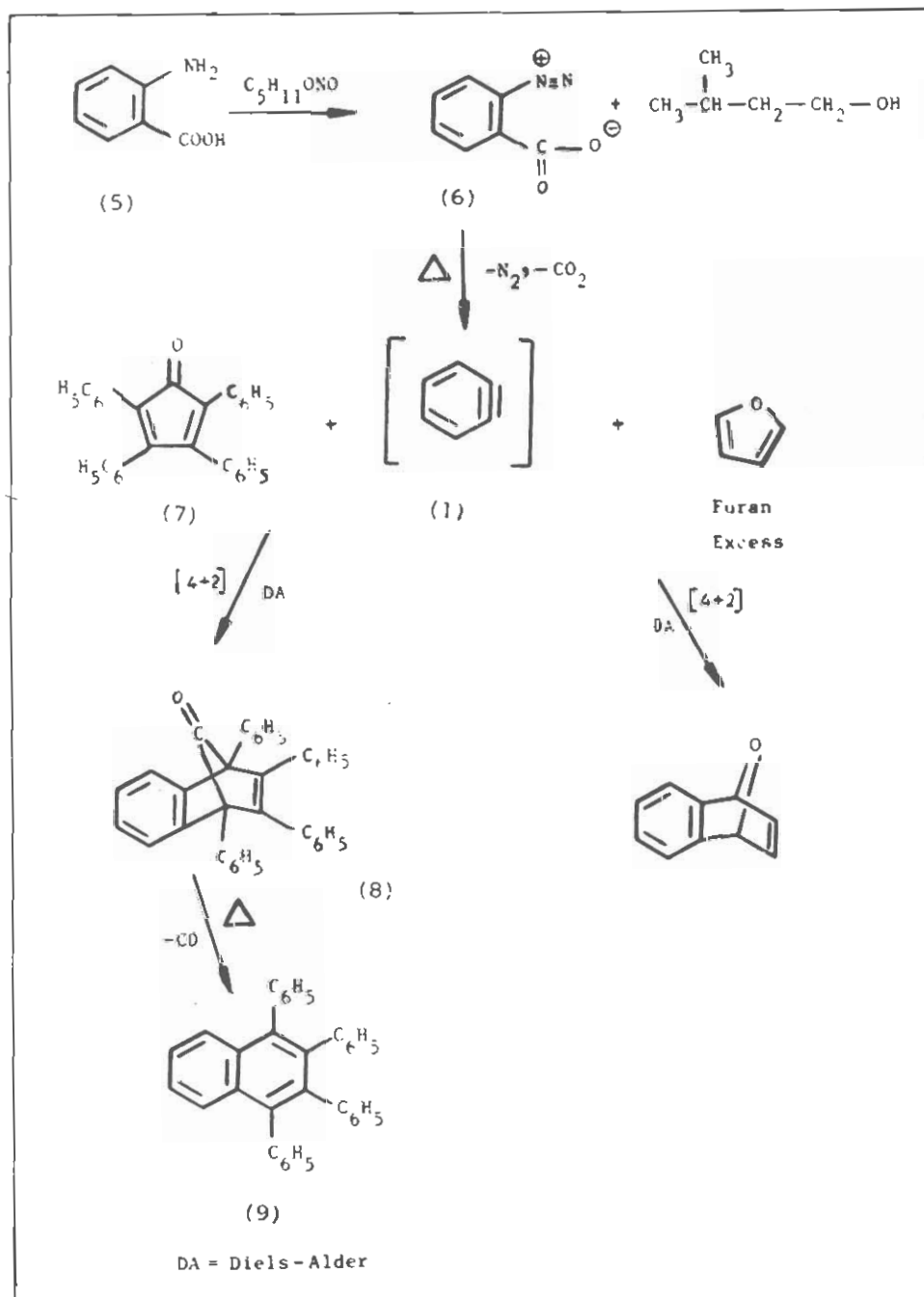


Fig. 1:  $^1\text{H NMR}$  spectrum of 1,2,3,4-tetraphenyl-naphthalene (9) in  $\text{CDCl}_3$  (60 MHz)

scheme 2



The  $^1\text{H}$ NMR spectrum shows four different kinds of aromatic protons and the IR spectrum shows  $\text{C}=\text{C}$  aromatic ring stretching, aromatic C-H out-of-plane bending and aromatic C-H stretching.

3,3'-Dicarboxy-4,4'-diaminobi-

phenyl (13) was synthesized and employed as starting material to generate the bisbenzyne. Compound (13) was made from o-nitrobenzoic acid (10) following standard procedures. Reduction of o-nitrobenzoic acid (10) with sodium hydroxide and

zinc dust yielded hydrazobenzene sodium-2,2'-dicarboxylate (11). Since it is a sodium salt, it stays in solution and was not isolated. Compound (11) is very sensitive to air (oxygen) and immediately oxidizes to an azo compound (-N=N-). This compound was used rapidly in a benzidine rearrangement reaction according to a previously described procedure [17] for the benzidine rearrangement and gave 3,3'-dicarboxylic acid benzenedihydrochloride salt (12) which is a white solid. This salt (12) was collected by suction filtration and since the yield was greater than theoretical, it was judged to be contami-

nated with sodium chloride (NaCl). To generate the free base and remove the sodium chloride, the salt (12) was dissolved in concentrated ammonia and then precipitated with glacial acetic acid which is the best way to acquire pure 3,3'-dicarboxy-4,4'-diaminobiphenyl (13). This reaction sequence is outlined in scheme 3.

The  $^1\text{H}$ NMR of free base (13) (Fig.2) shows a broad peak for  $-\text{NH}_2$ ,  $\text{COOH}$ , because of exchangeable protons, and peaks for aromatic protons. After adding  $\text{D}_2\text{O}$  to NMR tube, the broad peak disappeared and a peak belonging to water appeared at  $\delta=4.36$

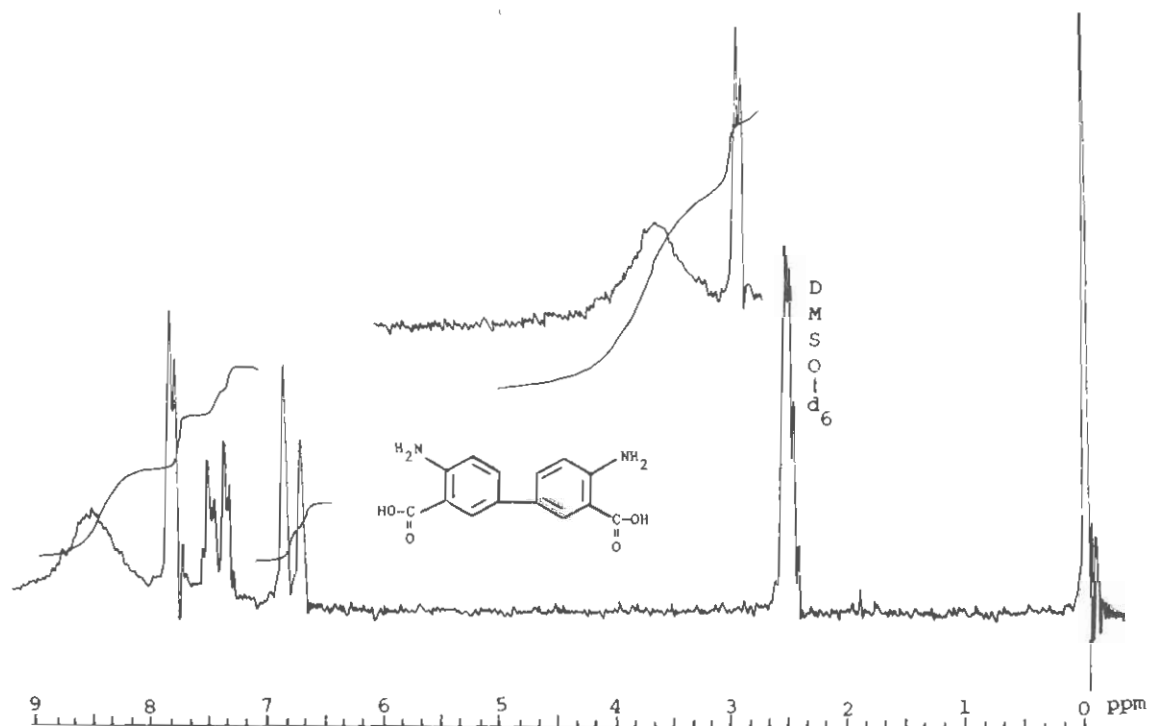
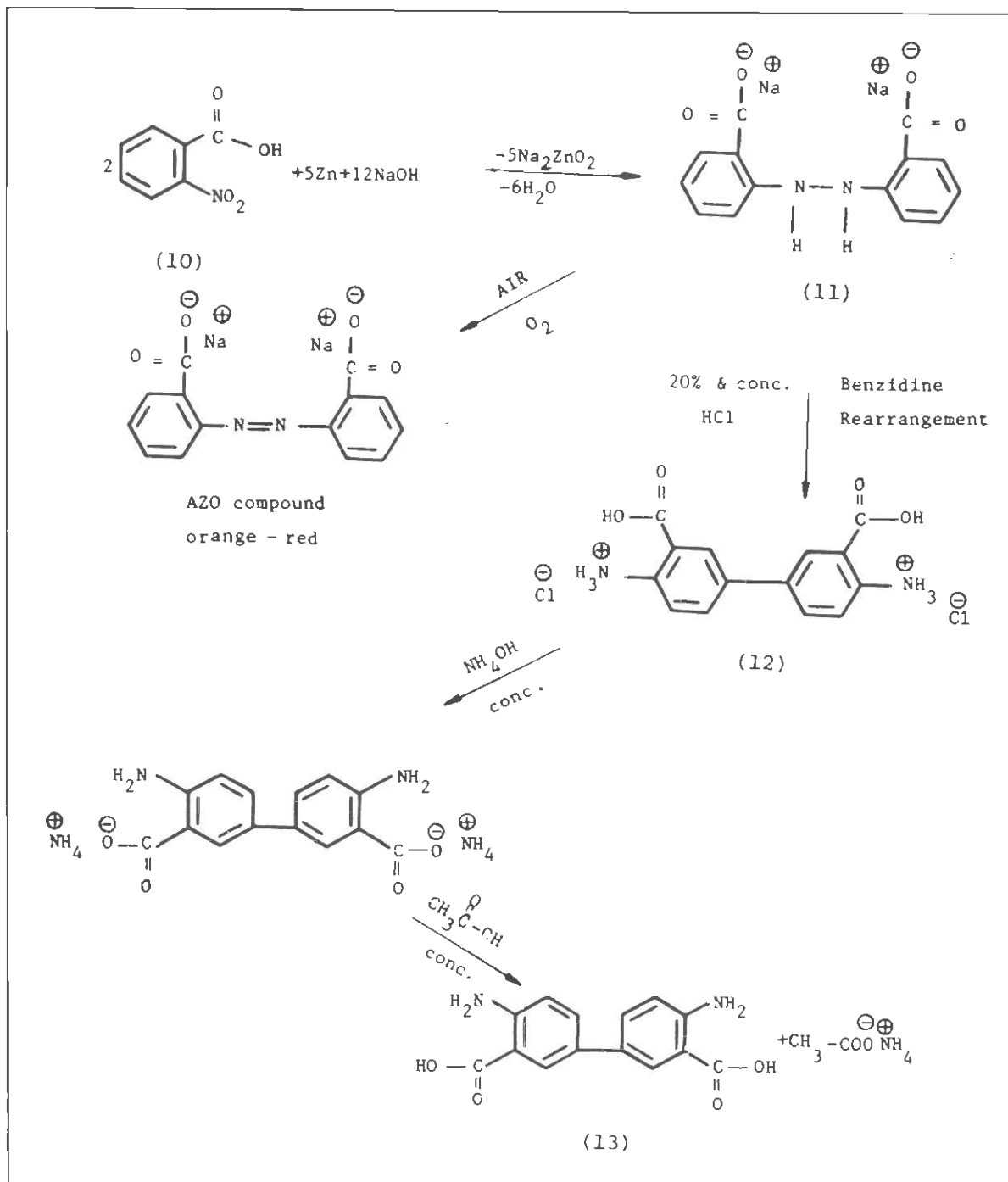


Fig.2:  $^1\text{H}$ NMR spectrum of 3,3'-dicarboxy-4,4'-diaminobiphenyl (13) in  $\text{DMSO-d}_6$  (60 MHz).

scheme 3



ppm. This is consistent with the occurrence of H/D exchange (Fig.3). The IR spectrum of compound (12) shows two peaks for  $-\text{NH}_2$  stretching, a broad peak for  $-\text{OH}$  stretching, because of hydrogen bonding, and  $\text{C}=\text{O}$  stretching.

Elemental analysis confirms its structure.

Aprotic diazotization in solution (1,2-dimethoxy ethane, DMSO) of 3,3'-dicarboxy-4,4'-diaminobiphenyl (13) with isoamyl nitrile gave biphenyl-4,

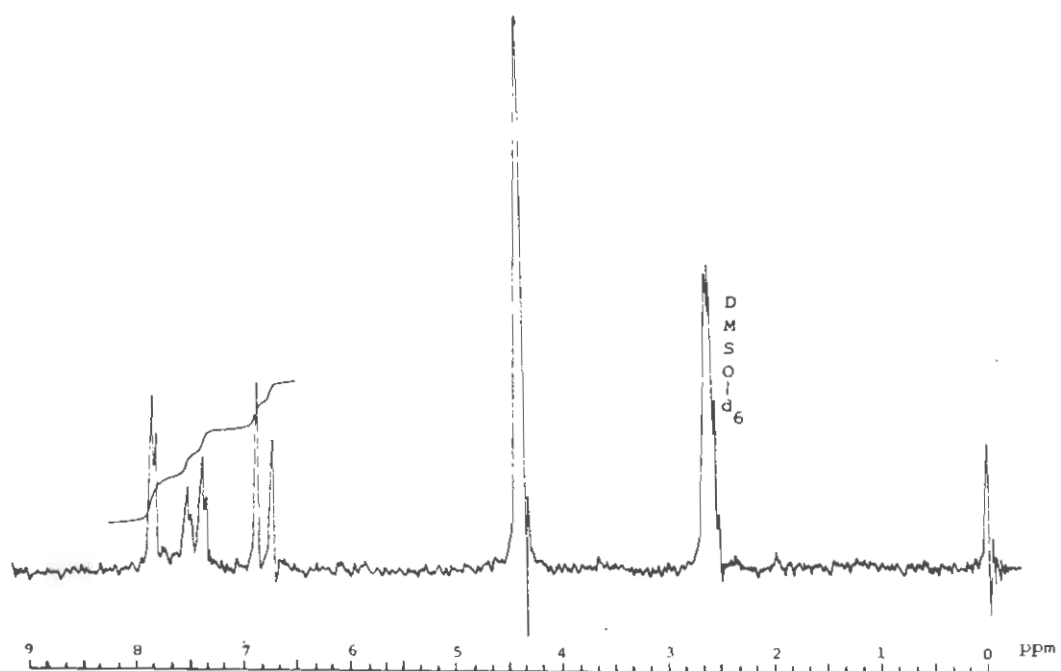


Fig. 3:  $^1\text{H}$ NMR spectrum of 3,3'-dicarboxy-4,4'-diaminobiphenyl (13) in  $\text{DMSO-d}_6, \text{D}_2\text{O}$ , (60 MHz).

4'-bisdiazonium-3,3'-dicarboxylate (14), and subsequent thermal ( $85^\circ\text{C}$ ) decomposition of (14) yielded the reactive intermediate 3,3',4,4'-tetra-dehydrobiphenyl (bisbenzyne) (4), nitrogen and carbon dioxide. This novel intermediate (4) was trapped with 2 moles of tetraphenylcyclopentadienone to give the previously unreported 5,6,7,8,5',6',7',8'-octaphenyl-2,2'-binaphthyl (15)\*. This compound is white in color and very soluble in chloroform; and shows no melting up to  $400^\circ\text{C}$ , as is expected from its structure (scheme 4).

The 3,3'-dicarboxy-4,4'-diaminobiphenyl (13) was found to be insoluble in most benzyne-producing

solvents; therefore, the diazotization reaction using (13) was run in a minimum amount of DMSO and resulted in rather poor yield of (15), 47%.

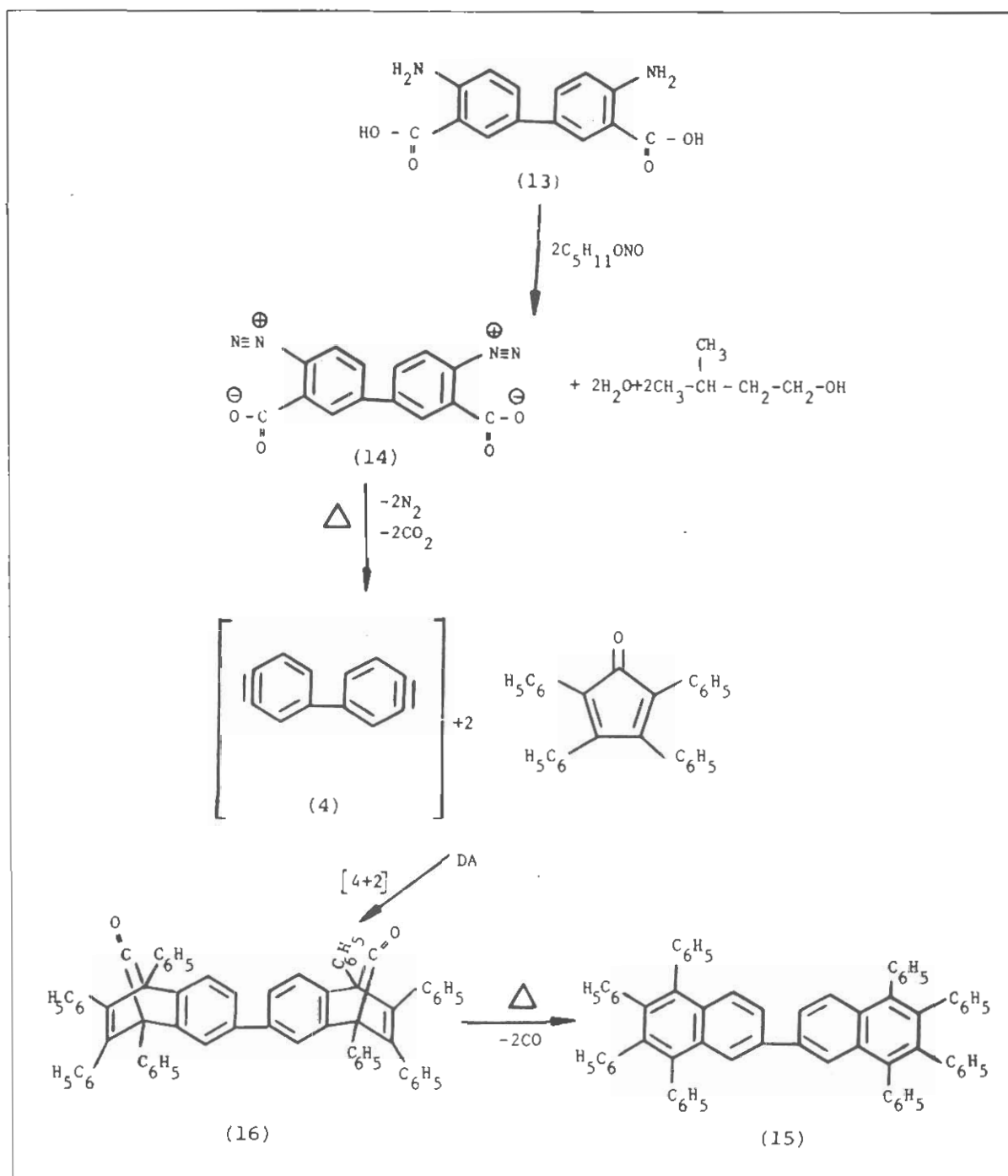
The  $^1\text{H}$ NMR spectrum (Fig. 4) of this new binaphthyl (15) shows almost the same pattern as the  $^1\text{H}$ NMR spectrum of that found for 1,2,3,4-tetraphenyl naphthalene, but the integration is 2:4:20:20 which shows the new compound has 46 hydrogens. Elemental analysis and IR spectrum also confirmed the structure of the new compound (15).

#### EXPERIMENTAL

Melting points were determined on an electrically heated melting point

\*The cyclic ketone intermediate not isolated, since it spontaneously lost CO to form the highly aromatic system (15).

scheme 4



(Melt-Temp) apparatus and are uncorrected. The Infrared spectra were recorded on Beckman model IR-8 spectrometer as either NUJOL MULLS or KBr pellets. The Nuclear Magnetic Resonance (NMR) spectra were deter-

mined by JEOL C-60HL NMR spectrometer with tetramethylsilane  $(\text{CH}_3)_4\text{Si}$  as an internal standard. Microanalysis was performed by spang Microanalytical Laboratory, star Route 1, Box 142, Eagle Harbor, Michigan 49951.



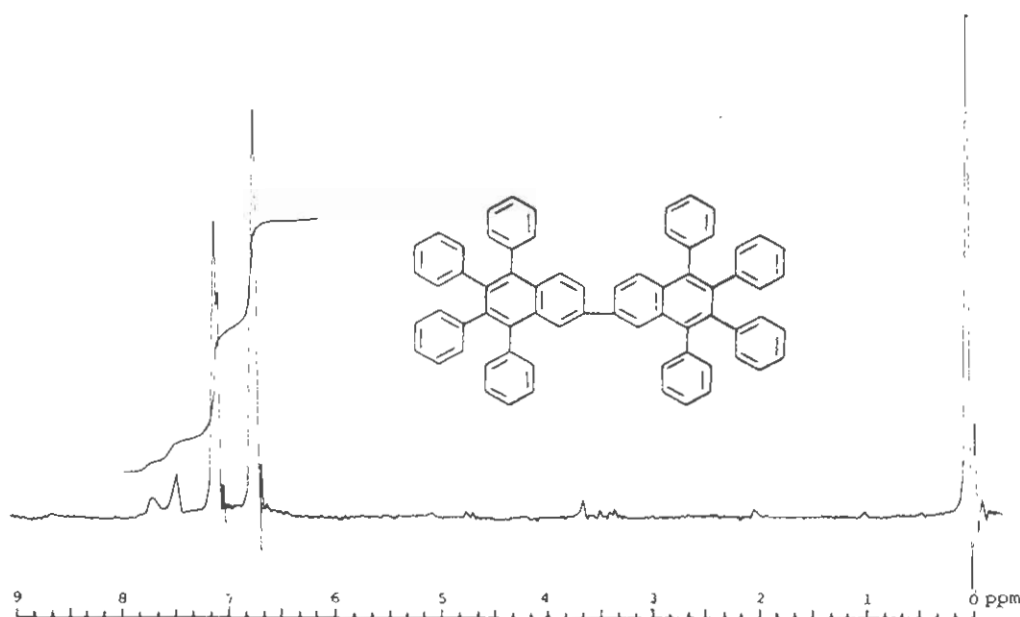


Fig.4:  $^1\text{H}$ NMR spectrum of 5,6,7,8,5',6',7',8'-octaphenyl-2,2'-binaphthyl (15) in  $\text{CDCl}_3$  (60 MHz).

Model compound synthesis:

*Synthesis of 1,2,3,4-Tetraphenyl-naphthalene (9) [15]*

Separate solution of 0.75 g (0.005 mole) of anthranilic acid and 2 ml of isoamyl nitrite each in 10 ml of 1,2-dimethoxy ethane, were added dropwise simultaneously to a stirred, refluxing solution of 1.92 g (0.005 mole) of dark-purple tetraphenylcyclopentadienone in 20 ml of 1,2-dimethoxy ethane over a period of about 1 hour. Refluxing was continued for 20 min after all reagents were added. Evaporation of the solvent with rotary evaporator and trituration of the yellowish residue with methanol gave 1.96 g (91%) of yellow solid m.p. 196-199°C. Recrystallization from 95% ethanol gave white prisms of sharp melting point 203-204°C.  $^1\text{H}$ NMR showed

peak: at  $\delta$  6.90 ppm (10H singlet, aromatic protons), 7.33 (10H singlet aromatic protons), 7.50 (2H multiplet,  $\text{H}_5 + \text{H}_8$ ), 7.66 (2H multiplet,  $\text{H}_6 + \text{H}_7$ ). IR showed peaks: at  $3049\text{ cm}^{-1}$  ( $3.28\ \mu\text{m}$ ),  $3021\text{ cm}^{-1}$  ( $3.32\ \mu\text{m}$ ) aromatic C-H stretching,  $1577\text{ cm}^{-1}$  ( $6.34\ \mu\text{m}$ )  $\text{C}=\text{C}$  aromatic ring stretching,  $1064\text{ cm}^{-1}$  ( $9.40\ \mu\text{m}$ ),  $1020\text{ cm}^{-1}$  ( $9.80\ \mu\text{m}$ ) in-plane C-H bending,  $741\text{ cm}^{-1}$  ( $13.5\ \mu\text{m}$ ), monosubstituted benzene, out-of-plane aromatic C-H bending,  $702\text{ cm}^{-1}$  ( $14.2\ \mu\text{m}$ ), monosubstituted, ring  $\text{C}=\text{C}$  bending.

*Synthesis of 3,3'-dicarboxy-4,4'-diaminobiphenyl (13) [18]*

*Preparation of hydrazobenzene sodium-2,2'-dicarboxylate*

Into a 1000 ml three-neck round bottomed flask containing 350 ml of 95% ethanol was added 30 g (0.180 mole) of O-nitrobenzoic acid and a solution

of 44.0g of sodium hydroxide in 100 ml of water all at once. The flask was fitted with a mechanical stirrer, condenser and thermometer. The mixture was heated by means of an electric heating mantle to 75-80°C and 75 g of activated zinc dust\* was added to the solution in 7-8 g portions. When the solution had become pale yellow an additional 100 ml of ethanol was added and the temperature was raised to boiling (2 hours), and filtered rapidly to avoid air oxidation through a previously warmed Bücher funnel. The sludge of zinc oxide collected on the funnel was washed with a small amount of hot ethanol. The basic pale yellow filtrate was transferred to a 1000 ml Erlenmeyer flask and cooled rapidly in an ice bath. Since the product at this point was a sodium salt, it remained in solution.

#### *Benzidine rearrangement*

This procedure was patterned after the procedure for preparing benzidine [17,19]. To the stirred, cooled hydrazobenzene sodium-2,2'-dicarboxylate solution in ethanol from above, 20% HCl (concentrated hydrochloric acid diluted with an equal volume of water), was added dropwise. The white 3,3'-dicarboxylic acid benzidine di-

hydrochloride (12) was precipitated, collected and transferred to a beaker containing 300 ml of ether. Addition of conc. HCl was continued to the filtrate until no more white precipitate was formed. To make sure that the benzidine rearrangement is complete, the white ether insoluble precipitate was transferred to a 1000 ml three-neck round-bottomed flask, cooled in ice bath. The flask was fitted with a mechanical stirrer. To this stirred solution 400 ml of concentrated HCl was added dropwise. After all HCl was added, the stirring was continued for 8 hours. The white 3,3'-dicarboxylic acid benzidine dihydrochloride was collected via suction filtration using a 350 ml medium sintered glass funnel. The weight of the product is 39.89 g, i.e. greater than the theoretical weight. It was thought that the product was contaminated with sodium chloride (NaCl).

To remove sodium chloride, 20 g of the hydrochloride salt was transferred to a 1000 ml beaker containing 300 ml of warm distilled water and was stirred for half an hour. The white-color salt turned to pale yellow color. The yellow solid was collected via suction filtration, and was washed with water, 5x20 ml portions. It was

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\* Since commercial zinc dust is occasionally found to be nonreactive, it was activated just prior to use by swirling with dilute hydrochloric acid following immediately by washing with water.

collected and vacuum dried. The IR spectrum (NH stretching) showed that the yellow solid is a free base.

The weight of product is 10 g 82% (based on O-nitrobenzoic acid). m.p. 250-270°C (d). It is slightly soluble in methanol, but quite soluble in dimethyl sulfoxide (DMSO) and N,N'-dimethylformamide (DMF). Pure 3,3'-dicarboxy-4,4'-diaminobiphenyl was obtained by dissolving the free base solid in concentrated ammonium hydroxide. To the ammonium salt solution glacial acetic acid was added until a precipitate was formed. The yellow precipitate was collected by suction, washed with water, 3x20 ml portions. The yellow solid was dried under vacuum, m.p. 290°C (d). <sup>1</sup>H NMR spectrum showed peaks: at δ 6.47-7.76 ppm (6H multiplet, aromatic protons), at 8.5 ppm (6H broad because of strong hydrogen bonding and exchangeable protons, 2-NH<sub>2</sub>, 2-C-O-H). IR spectrum showed peaks: at 3497 cm<sup>-1</sup> (2.86 μm) asymmetric N-H stretching, 3367 cm<sup>-1</sup> (2.97 μm) symmetric N-H stretching, 3279-2381 cm<sup>-1</sup> (3.05 μm-4.20 μm) broad O-H stretching, 1639 cm<sup>-1</sup> (6.10 μm) C=O stretching, 1538 cm<sup>-1</sup> (6.50 μm) C-C ring stretching.

Anal. for C<sub>14</sub>H<sub>12</sub>N<sub>2</sub>O<sub>4</sub> :

Calcd: C, 61.76% ; H, 4.44% ; N, 10.29%.

Found: C, 61.84% ; H, 4.40% ; N, 10.30%.

#### Generation and trapping bisbenzynes: *Synthesis of 5,6,7,8,5',6',7',8'-Octaphenyl-2,2'-Binaphthyl (15)*

In a 250 ml three-neck round-bottomed flask, fitted with a water cooled condenser was added 2.85 g (0.0074 mole) of dark purple tetraphenylcyclopentadienone along with 40 ml of 1,2-dimethoxy ethane, and a magnetic stirring bar. The flask was heated electrically with a mantle. The wine-red solution started refluxing (85°C). Solutions of 1.0g (0.0037 mole) of 3,3'-dicarboxy-4,4'-diaminobiphenyl in 10 ml of dimethyl sulfoxide (DMSO), 13 ml of 1,2-dimethoxy ethane, and 2 ml of isoamyl nitrite in 20 ml of 1,2-dimethoxy ethane were added dropwise simultaneously to the refluxing mixture over a period of 2 hours. Refluxing was continued for 4 hours. The wine-red solution turned to a brown color. The flask was fitted for distillation and the brown solution was concentrated to approximately 20 ml by distillation process. The flask was cooled and a yellow precipitate formed which was collected by suction filtration using a sintered glass funnel. The weight of the crude product is 1.5 g (47%). The yellow solid was transferred to 100 ml of methanol and 50 ml of dioxane for recrystallization whereupon cooling white crystals were recovered. It does not melt at 400°C. IR spectrum

showed peaks: at  $3049\text{ cm}^{-1}$ ,  $3125\text{ cm}^{-1}$  ( $3.28\text{ }\mu\text{m}$ ,  $3.32\text{ }\mu\text{m}$ ) aromatic C-H stretching,  $1585\text{ cm}^{-1}$ ,  $1471\text{ cm}^{-1}$  ( $6.32\text{ }\mu\text{m}$ ,  $6.80\text{ }\mu\text{m}$ ) C=C ring stretching,  $1064\text{ cm}^{-1}$ ,  $1020\text{ cm}^{-1}$  ( $9.40\text{ }\mu\text{m}$ ,  $9.80\text{ }\mu\text{m}$ ) in-plane C-H bending, etc. NMR spectrum showed peaks: at  $\delta 6.71, 7.08, 7.50, 7.72$  ppm. All aromatic protons.

Anal. for  $\text{C}_{68}\text{H}_{46}$ :

Calcd: C, 94.63%; H, 5.37%.

Found: C, 94.30%; H, 5.63%.

## CONCLUSION

The aprotic diazotization of 3,3'-dicarboxy 4,4'-diaminobiphenyl gave biphenyl-4,4'-bisdiazonium-3,3'-dicarboxylate. The subsequent thermal decomposition of this diazonium in solution produced the bisbenzyne intermediate which was trapped with tetraphenylcyclopentadienone via a [4+2]Diels-Alder cycloaddition reaction yielding the previously unreported 5,6,7,8,5',6',7',8'-octaphenyl-2,2'-binaphthyl. It is possible and interesting to consider in the future possibilities that this bisbenzyne may act as a bifunctional molecule (monomer) in a step-growth polymerization reaction, either with other monomers such as bisdienes or with itself to yield a polybiphenylene.

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