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## Buttressing Effect in 3, 3' -Disubstituted-2, 2' -Three-Carbon-Atom Bridged Biphenyls

Yunn Hui Chiang

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BUTTRESSING EFFECT  
IN  
3,3'-DISUBSTITUTED-2,2'-THREE-CARBON-ATOM  
BRIDGED BIPHENYLS

Dissertation

Submitted in Partial Fulfillment

of the Requirements for the Degree of

Master of Arts in Chemistry

to the

Faculty of the Graduate School

of

Western Michigan University

By

Chiang, Yunn Hui, B.S.

Kalamazoo

Michigan

1961

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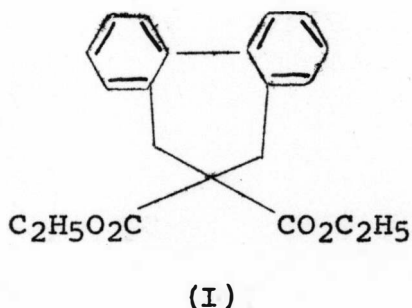
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## INTRODUCTION

The configuration of biphenyl has been the subject of much investigation and many recent reviews (1, 5, 6, 7, 8, 17, 21, 22). Of particular interest has been the configuration of 2,2'-bridged biphenyl derivatives. The preparation of an optically active 2,2'-three-carbon-atom-bridged biphenyl having an ultraviolet absorption maximum at 250 mμ, has been recently described (14). Although the compound was easily racemized, this property requires that a non-planar configuration be assigned to this biphenyl (I). Furthermore, this ultraviolet spectra indicates that inter-ring conjugation must exist in the non-planar configuration.



Ahmed and Hall (2,3) have prepared a series of 2,2'-three-atom-bridged biphenyls in order to obtain a representative measure of specific rotation of these bridged compounds. Various 6,6'-substituents larger than the

hydrogen atom were introduced in order to increase optical stability of the compounds studied. It was reasoned that an alternate approach in changing the structure to increase optical stability would be to employ the buttressing effect of bulky 3,3'-disubstituents to increase the rigidity of the three-atom bridge. By this latter method, the change in configuration should be less pronounced with change in size of the new substituent and should permit a study of the effect of small changes in the twist angle between the benzene rings in biphenyl derivatives.



## EXPERIMENTAL

In the following section, all boiling and melting points are in degrees Centigrade and are uncorrected. The micro-analytical data were obtained from the Galbraith Laboratories, Knoxville, Tennessee.

The ultraviolet absorption spectra were obtained on a Beckman Model DU spectrophotometer. The solvent for all spectral measurements was 95% ethanol.

### Preparation of ammonium hydrogen 3-nitrophthalate, III

Following the procedure described by Kahn (16), 1.75 moles of 3-nitrophthalic acid was converted to the monoammonium salt in 94% yield.

### Preparation of 3-nitrophthalimide, IV

Three and three-tenths moles of the monoammonium salt of 3-nitrophthalic acid was changed to 3-nitrophthalimide by heating according to the method of Kahn (16). A 95% yield of amide was obtained: m.p. 220-221°. Lit.: m.p. 215-216°.

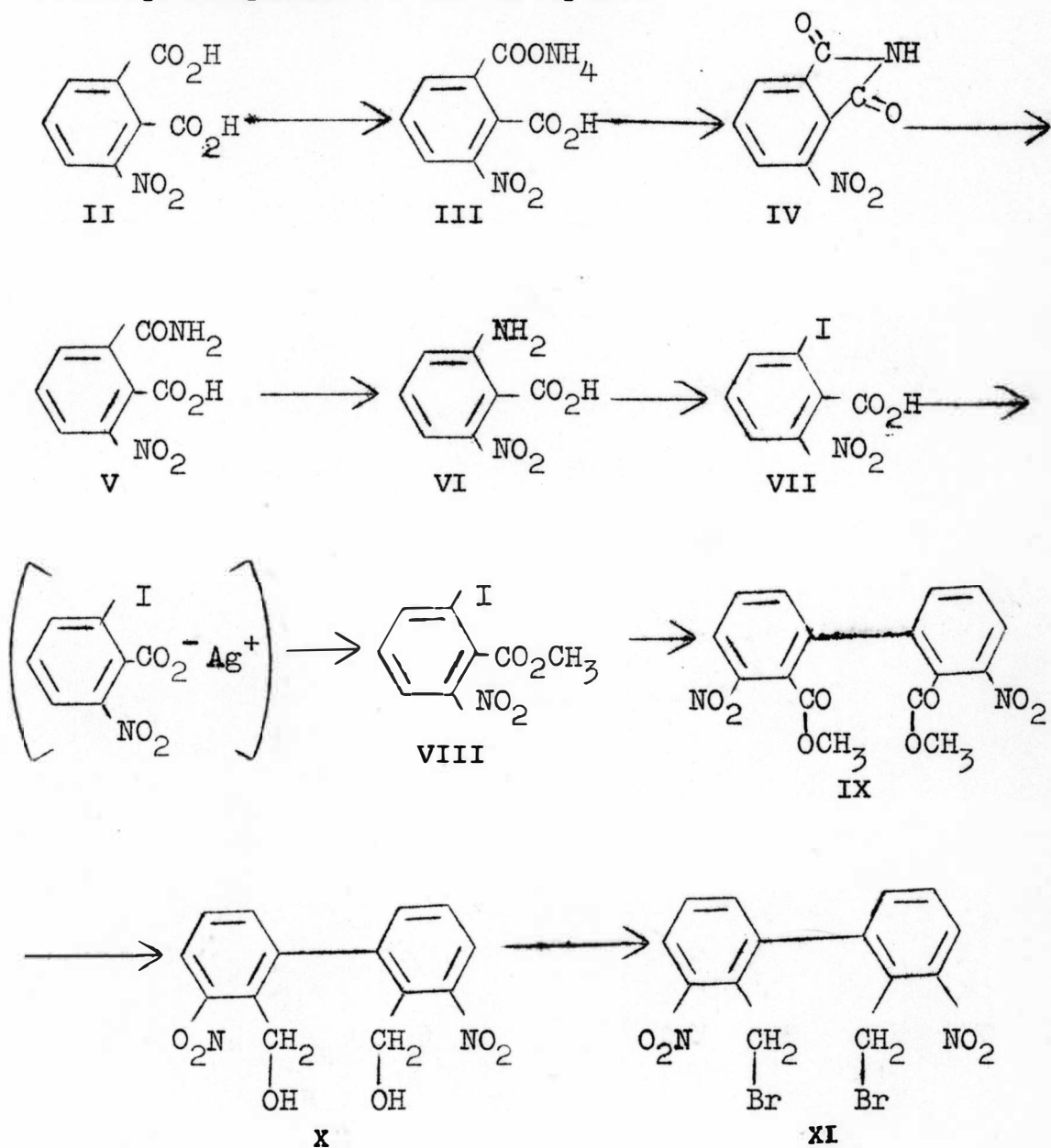
### Preparation of 3-nitrophthalamidic acid, V

One-quarter mole quantities of 3-nitrophthalimide were hydrolyzed with a slight excess of 0.5 N aqueous sodium

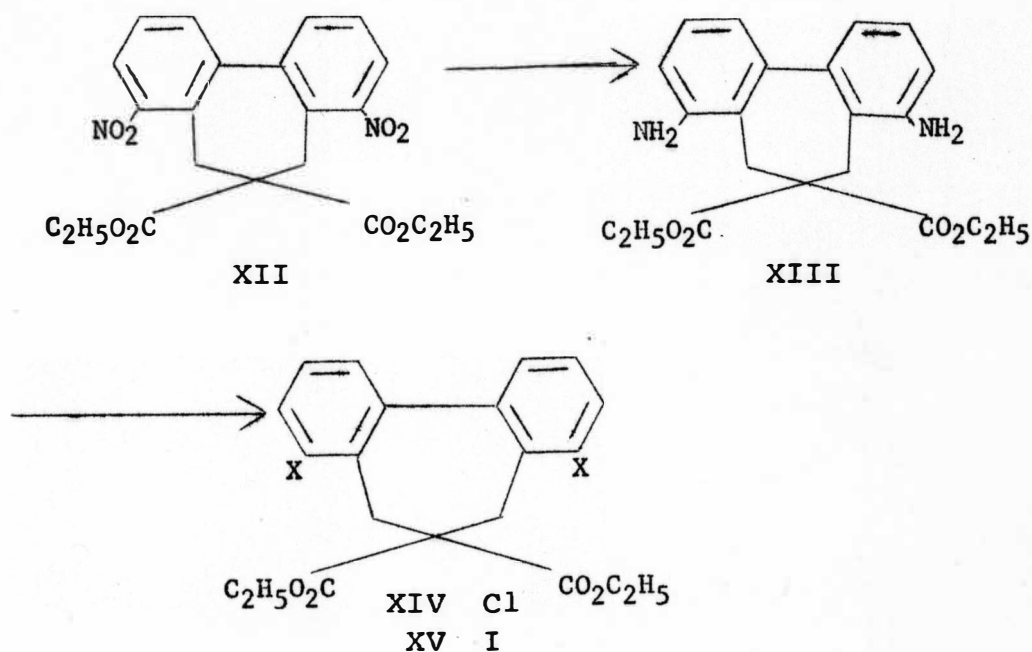
## Chart I

## Plan I

Synthesis of Diethyl 4,8-disubstituted-5,7-dihydrodibenzo  
[a,c]cycloheptene-6,6-dicarboxylate



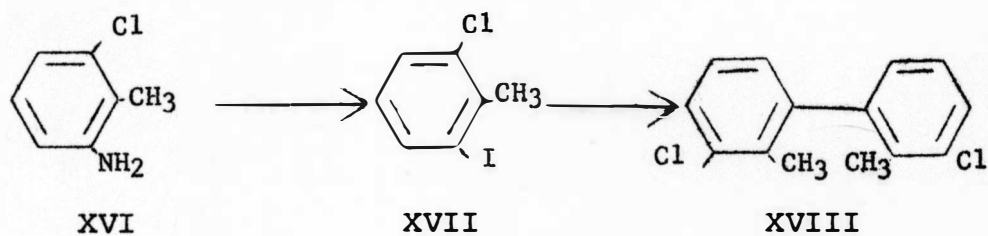
## Chart I, Plan I (continued)



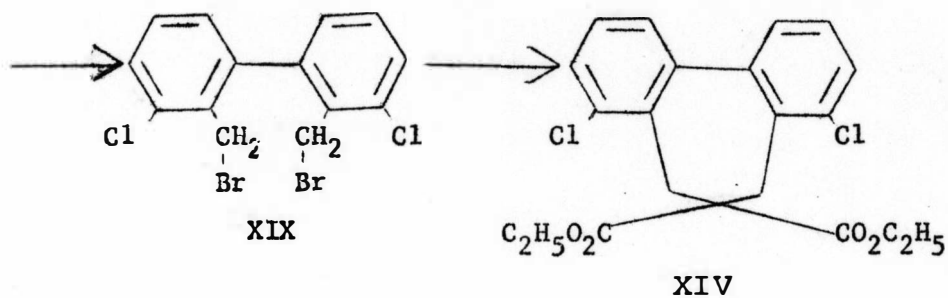
## Chart II

## Plan II

Synthesis of diethyl 4,8-dichloro-5,7-dihydrodibenzo [a,c] cycloheptene-6,6-dicarboxylate

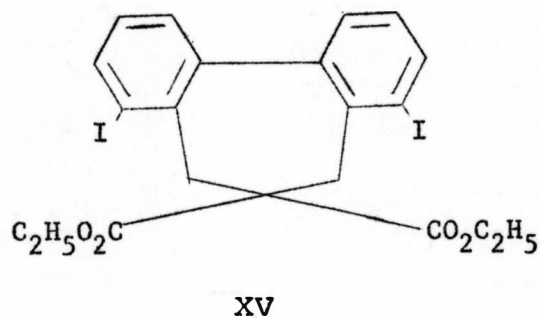
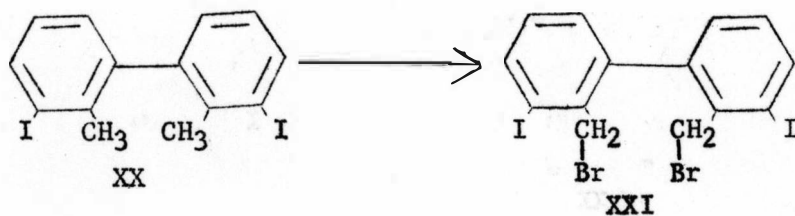
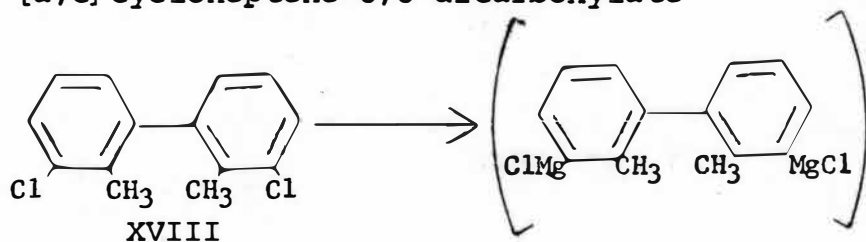


## Chart II, Plan II (continued)



## Chart III

Synthesis of diethyl 4,8-diiodo-5,7-dihydrodibenzo [a,c] cycloheptene-6,6-dicarboxylate



hydroxide as reported by Kahn (16). A 70% yield of 3-nitrophthalamidic acid was obtained: m.p. 158-159°. Lit.: 158-159°. Hydrolysis attempts with more concentrated sodium hydroxide solution led to a marked decrease in yield.

#### Preparation of 6-nitroanthranilic acid, VI (10)

The following procedure for the Hofmann reaction was developed according to the recommendations of Wallis and Lane (22).

Two-hundredths mole (4.5 g.) of the amide (<sup>IV</sup>~~IX~~) was dissolved in 50 ml. of 0.5 N sodium hydroxide. The solution was filtered and cooled to 5°. Thirty-five grams of Roman Cleanser solution (equivalent to 1.85 g., 0.025 mole, of NaClO) containing 2.0 g. (0.05 mole) of sodium hydroxide was added. The reaction mixture was warmed to 70-85° for fifteen minutes, then cooled to 0° and acidified with 2 N hydrochloric acid until the solution turned yellow (pH = 3-4). On cooling, a red-brown precipitate was obtained and weighed 3.0 g. (85%): m.p. 187-189°. Lit.: 183-184°.

When the procedure was increased to 0.5 to 1.5 moles of amide, the yield invariably fell to 30-60%, and the product melted over a broad range (as low as

160°).

#### Preparation of 6-nitro-2-iodobenzoic acid, VII

Seventeen-hundredths mole (12.16 g.) of sodium nitrite was added to a solution containing 29.0 g. (0.16 mole) of 3-nitroanthranilic acid and 8.48 g. (0.08 mole) of anhyd. sodium carbonate in 200 ml. of water. The resulting solution was poured onto a mixture of 138 ml. of 36% hydrochloric acid and 200 g. of ice to effect diazotization as described by Boken and coworkers (9). After removing the excess nitrous acid with urea, the cold solution was poured into a solution of 105.6 g. (0.63 mole) of potassium iodide. After heating on steam, free iodine was removed by adding sodium bisulfite and the oil was separated and solidified on standing at 3°. Recrystallization from water gave 20.0 g. (70%) of 6-nitro-2-iodobenzoic acid: m.p. 181-183°. Lit.: m.p. 181-183°.

#### Preparation of methyl 6-nitro-2-iodobenzoate, VIII

According to Rule & Smith (19), 0.01 mole (2.90 g.) of the iodo acid was changed to the silver salt, which then was reacted with methyl iodide to yield the methyl ester. Recrystallization from aqueous methanol gave

2.5 g. (80%) of the ester: m.p. 94-96°. Lit.: m.p. 94°.

Preparation of dimethyl 3,3'-dinitrodiphenate, IX

Two-hundredths mole (6.14 g.) of the iodo-ester (VIII) was dissolved in 20 ml. of dimethylformamide (dried over calcium hydride). The solution was heated to boiling and 1.6 g. (0.025 g. at. wt.) of copper powder prepared from cupric sulfate (13) was added. After refluxing for 2 hours, another 1.6 g. portion of the copper powder was added. Refluxing was continued for another 2 hours. On cooling, the reaction mixture was poured into 500 ml. of acetone and treated with decolorizing carbon, concentrated to about 50 ml. and 150 ml. of water was added. A precipitate formed during storage over night at 5° and was recrystallized from methanol. A 90% yield (3.20 g.) of the product was obtained: m.p. 145-147°. Anal. calculated for  $C_{16}H_{12}N_2O_8$ : N, 7.78. Found: N, 7.69.

Preparation of 6-chloro-2-iodotoluene, XVII (11)

One mole (142.0 g.) of 3-chloro-2-methylaniline (D.P.I. No. P 5245) was added to 400 ml. of water and 450 g. (4.5 mole) of hydrochloric acid (36%) was added. The amine hydrochloride precipitated. The solution was cooled to 5° and stirred thoroughly while 84 g. (1.22

mole) of sodium nitrite dissolved in the minimum amount of water was slowly added. The addition was completed in 2 to 3 hours and the amine salt disappeared. The excess sodium nitrite was destroyed by the reaction with urea. After filtration of the diazonium salt solution, 250 g. (1.52 mole) of potassium iodide in 350-400 ml. of water was added. A red precipitate was obtained. The reaction mixture was warmed to room temperature; the precipitate violently decomposed forming a black oil. The oil layer was separated and washed with water. After drying with anhydrous sodium sulfate and distillation, 192 g. (75%) of the product was obtained: b.p. 99-100° at 5 mm;  $n_D^{25}$  1.6255. Lit.: b.p. 132-133° at 25 mm.

#### Preparation of 3,3'-dichloro-o,o'-bitolyl, XVIII

One mole (255 g.) of XVII, 2 g. at. wt. (126 g.) of copper and about 3 teaspoons of white sand were contained in a 500 ml. three neck flask fitted with reflux condenser and motor driven stirrer. The mixture was stirred at reflux temperature (220-240°) for 75 hours. After cooling to room temperature, the oil was removed and the solid portion was extracted thoroughly with benzene. The benzene solution was treated with



decolorizing carbon and the benzene was removed by distillation. The residue was distilled under reduced pressure. After collection of a small amount of unreacted iodo compound, the product was collected: 133-139° at 2 mm. The distilled material solidified and was recrystallized from methanol. A 75% yield (93.9 g.) of XVIII was obtained: m.p. 75-76°. The ultraviolet absorption spectra is shown in Fig. I. Anal. calculated for  $C_{14}H_{12}Cl_2$ : C, 66.95; H, 4.82. Found: C, 66.74; H, 4.99.

Preparation of  $\alpha, \alpha'$ -dibromo-3,3'-dichloro-o,o'-bitolyl, XIX

Six-hundredths mole (15 g.) of XVIII was dissolved in 150 ml. of carbon tetrachloride and 45 g. (0.253 mole) of N-bromosuccinimide was added to the solution. After heating to boiling, 1 g. of benzoyl peroxide was added and refluxing was continued for 18 hours. A second 1.5 g. portion of benzoyl peroxide was added. Refluxing was continued for another 24 hours. The reaction mixture was filtered while the solution was hot. The filtrate was twice washed with 1 to 2% aqueous sodium bisulfite solution and dried with anhyd. sodium sulfate. After removing the carbon tetrachloride, the

residue was chromatographed on neutral alumina using petroleum ether (60-110°) as eluent. The solvent was evaporated under a current of air. The precipitate was collected and crystallized from petroleum ether (60-110°). A 71% yield (17.9 g.) of the dibromide was obtained: m.p. 120-121°. Anal. calculated for  $C_{14}H_{10}Cl_2Br_2$ : C, 41.11; H, 2.46. Found: C, 41.26; H, 2.55.

Preparation of diethyl 4,8-dichloro-5,7-dihydrodibenzo [a,c] cycloheptene-6,6-dicarboxylate, XIV

One hundred ml. of absolute ethanol was placed into a 300 ml. three neck flask fitted with condenser and 1.84 g. (0.08 g. at. wt.) of freshly cut sodium was added. After the sodium was completely dissolved, the solution was cooled to room temperature and 6.4 g. (0.04 mole) of diethyl malonate was added; after 5 to 10 minutes, a white precipitate was obtained. This suspension was transferred to an addition funnel and added dropwise with stirring to a solution containing 8.2 g. (0.02 mole) of  $\alpha,\alpha'$ -dibromo-3,3'-dichloro-o,o'-bitolyl dissolved in 40 ml. of warm dioxane. Addition was completed in one hour and the reaction mixture was heated on steam for 5 hours with stirring. Ice-water

was added and a white precipitate was obtained. After filtration, the precipitate was recrystallized from 95% ethanol to yield 5.86 g. (72%) of white crystalline plates: m.p. 150-151°. The ultraviolet absorption spectra is shown in Fig. II:  $\lambda_{\max}$  250 m $\mu$ ;  $\log \epsilon_{\max}$  4.18. Anal. calculated for  $C_{21}H_{20}O_4Cl_2$ ; C, 61.92; H, 4.95. Found: C, 61.75; H, 4.71.

#### Preparation of 3,3'-diiodo-o,o'-bitolyl, XV

A solution of 50.4 g. (0.2 mole) of 3,3'-dichloro-o,o'-bitolyl dissolved in 500 ml. of tetrahydrofuran (THF) (dried over calcium hydride) was prepared. Several iodine crystals and 9.8 g. (0.4 g. at. wt.) of magnesium turnings were added. If the reaction did not start after 10 to 12 hours, additional iodine crystals were added and refluxing was continued.

The solution was refluxed for 44 hours. During this time, a turbidity developed (due to the Grignard reagent). This suspension was transferred into an addition funnel and added to a solution containing 127 g. (0.5 g. at. wt.) of crystalline iodine dissolved in 500 ml. of THF. The Grignard reagent suspension

was added dropwise to the iodine solution during a three-hour period. After adding about 500 ml. of ice-water, the unreacted magnesium was collected and weighed 5.18 g. After reacting the excess iodine with sodium bisulfite, the THF was removed by distillation. The water mixture remaining was extracted with benzene. After drying with anhyd. sodium sulfate, the benzene solution was treated with decolorizing carbon, concentrated, and cooled in an ice bath. A solid was obtained only after crystallization was induced by scraping with a glass rod. The white solid obtained was recrystallized from methanol; 30.65 g. (35%) of product was collected: m.p. 119-120°. The ultraviolet absorption spectra is shown in Fig. I. Anal. calculated for  $C_{14}H_{12}I_2$ : C, 38.73; H, 2.79. Found: C, 38.98; H, 2.79.

Preparation of  $\alpha,\alpha'$ -dibromo-3,3'-diiodo-o,o'-bitolyl, XVI

Twelve grams (0.028 mole) of the 3,3'-diiodo-o,o'-bitolyl was dissolved in 150 ml. of carbon tetrachloride and brominated with 11 g. (0.062 mole) of N-bromosuccinimide, similar to the reaction with the dichlorobitolyl. The hot reaction mixture was filtered

and washed with aqueous sodium bisulfite solution.

The carbon tetrachloride solution was dried with anhyd. sodium sulfate and concentrated. Cooling with ice gave 14.11 g. (86%) of powder product: m.p. 159.5-160.5°. A sample was recrystallized from carbon tetrachloride for analysis. Anal. calculated for  $C_{14}H_{10}I_2Br_2$ : C, 28.38; H, 1.78. Found: C, 28.41; H, 1.70.

Preparation of diethyl 4,8-diiodo-5,7-dihydrodibenzo [a,c] cycloheptene-6,6-dicarboxylate, XV

A solution of sodium ethoxide was prepared by adding 0.8 g. (~~0.0035~~ 0.0035 g. at. wt.) of sodium to 50 ml. of absolute ethanol. After cooling, 1.36 g. (0.0085 mole) of diethyl malonate was added. After 5 to 10 minutes, a white precipitate was formed. After transferring to an addition funnel, this suspension was added dropwise to a solution of 5.0 g. (0.0085 mole) of dibromo compound (XXI) dissolved in 40 ml. of warm dioxane. Addition was continued for one hour. The mixture was heated on a steam bath for 5 hours. Ice-water was added. An excess of water was added in order to cause the product to separate from the aqueous dioxane solution. The mixture was extracted

with ethyl ether and dried over anhyd. sodium sulfate. The ether was evaporated under reduced pressure. After the residue was recrystallized from a ethanol-water mixture, 1.90 g. (38%) of product was obtained: m.p. 53-55°. The ultraviolet absorption spectra failed to show an absorption maximum in the 250 mμ region and is summarized in Fig. II. Anal. calculated for  $C_{21}H_{20}O_4I_2$ : C, 42.73; H, 3.42. Found: C, 42.87; H, 3.60.

In the first attempt with this reaction, 0.01 mole of the dibromide was reacted with 0.02 mole of diethyl malonate according to the procedure described for the  $\alpha, \alpha'$ -dibromo-3,3'-dichloro-o,o'-bitolyl. A 16% yield of the expected product was isolated having the properties indicated above. Repetition on a 0.017 mole scale led, however, only to the isolation of an anomalous product which melted at 224-225° and provided the following analytical value: Anal. calculated for  $C_{28}H_{32}O_8I_2$  (XXII, cf. p. <sup>23</sup>~~16~~): C, 47.07; H, 4.30. Found: C, 44.50; H, 3.87.

#### Attempted preparation of 3,3'-dibromo-o,o'-bitolyl

The Grignard reagent was prepared from 0.1 mole of 3,3'-dichloro-o,o'-bitolyl according to the procedure

described on page 11 and added to a solution containing 40 g. (0.25 g. at. wt.) of bromine dissolved in 200 ml. of THF. The Grignard reagent suspension was added dropwise to the bromine solution during a 2 hour period. The mixture was stirred over night. After adding about 300 ml. of ice-water, the excess bromine was destroyed by reacting with sodium bisulfite and the THF was removed by distillation. The water mixture remaining was extracted with benzene and dried with anhyd. sodium sulfate. The dried solution was concentrated, and the residue oil was chromatographed on neutral alumina using benzene, 5% methanol-benzene solution and methanol as eluents. The benzene and mixed solvent fraction were combined and dissolved in 230 ml. of petroleum ether (30-60°). The mixture was filtered; the filtrate was treated with decolorizing carbon, and the solvent was removed under reduced pressure. The residue was distilled under reduced pressure; b.p. 94-102°, weight 19.41 g.,  $n_D^{24}$  1.5588. These properties correspond to those reported for o,o'-bitolyl. This identification was confirmed by gas chromatograph comparison with authentic o,o'-bitolyl. No 3,3'-dibromo-o,o'-bitolyl was isolated.

## DISCUSSION AND CONCLUSION

Two plans for the synthesis of diethyl 4,8-disubstituted-5,7-dihydro-di-benzo [a,c] cycloheptene-6,6-dicarboxylate were investigated. Plan one, summarized in <sup>CHART</sup> ~~Table~~ I, was based upon reasonable and analogous reaction steps already reported in the literature and led to the 4,8-dinitro derivative. Although this sequence of reactions was lengthy, the yields to be expected in each step were high. Furthermore, reduction of the dinitro compound followed by a Sandmeyer reaction would provide a variety of new 4,8-disubstituted derivatives.

In small scale pilot experiments, good yields were realized in each step starting from 3-nitrophthalic acid (II) to dimethyl 3,3'-dinitro-2,2'-diphenate. However, in the large scale experiments necessary for the preparation of reasonable amounts of the final product, it was impossible to maintain good yields in the Hofmann reaction. This reaction according to Kahn (16) gave good results. In this study, the reaction was tried five times using potassium hypobromite with unsatisfactory results in each case. The reaction



appeared very sensitive to temperature and pH in the isolation stage. In the small preparation, a yield as high as 49% was obtained. On the larger scale, because of difficulty in controlling these reaction conditions, the yield was poor. With the use of sodium hypochlorite, the above reaction conditions were less critical, and the yield and the quality of amine (VI) were improved. The yield in the small scale was as high as 84%; however, in the 0.5 mole scale reactions, the yield was again low (30-60%).

For this reason along with the relatively high cost of 3-nitrophthalic acid (D.P.I. No. 3809) consideration was given to alternate routes to the 3,3'-disubstituted biphenyl derivatives. The low cost and availability of 3-chloro-2-methyl aniline (D.P.I. No. P 5245) and the simplicity of the sequences of reactions in plan II made this route attractive for the preparation of at least one of the desired 3,3'-disubstituted biphenyls. Difficulty was anticipated in the conversion of the 3,3'-dichloro substituents to other larger atoms and groups. Success was obtained in formation of the 3,3'-diiodo-o,o'-bitolyl via the di-Grignard intermediate. In this way, the diethyl

4,8-diiodo-5,7-dihydrobenzo [a,c] cycloheptene-6,6-dicarboxylate was prepared as indicated in Table III. The analogous preparation of 3,3'-dibromo-o,o'-bitolyl was unsuccessful.

The first instance, using the Ullman reaction, was encountered in plan I where dimethylformamide (b.p. 154°) was used as reaction solvent according to the method of Kornblum and Kendall (18) with a 90% yield of the dimethyl 3,3'-dinitro-2,2'-diphenate resulting. Activated copper prepared by reduction of cupric sulfate with zinc was used.

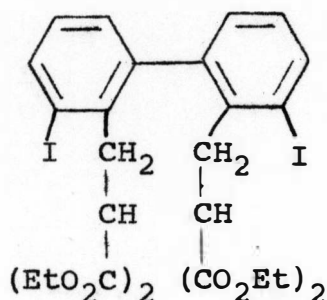
In the second Ullman reaction in plan II, the reaction of 6-chloro-2-iodo-toluene, with either precipitated copper or electrolytic copper, gave only a 30% yield of 3,3'-dichloro-o,o'-bitolyl using dimethylformamide solvent. It was reasoned that a higher reaction temperature would be helpful. Accordingly, the reaction was repeated without solvent and a reaction temperature at 220-240°. The yield increased to 75% when either type of copper was used. The effect of temperature was further demonstrated in an experiment at 190-200° resulting in only a 40% yield of Ullmann reaction product.

In the thorough review of reactions of Grignard reagents by Kharash and Reimmuth (15), there is reported one example of the reaction of an aryl magnesium bromide with halogen to effect formation of an aryl halide. Thus, Datta and Mitter reported in 1919 (12), the addition of phenyl magnesium bromide to an ether solution of iodine to form iodobenzene in 90% yield. This reaction thus provided a potential route from the 3,3'-dichloro-o,o'-bitolyl to other 3,3'-dihalogen derivatives.

Accordingly, the Grignard reagent of the 3,3'-dichloro-o,o'-bitolyl was prepared in tetrahydrofuran solution (THF) and added to a THF solution of iodine. Although results of four experiments were variable, yields of 3,3'-diiodo-o,o'-bitolyl as high as 35% were obtained. It is believed that quality of the THF is extremely critical in the preparation of the Grignard reagent and the best yields were obtained with THF that had been dried at least 12 hours over calcium hydride. The reaction with iodine is mildly exothermic and the best yield was obtained with the reaction above room temperature but below reflux temperature of the solvent.

Two attempted syntheses of 3,3'-dibromo-o,o'-bitolyl by this exchange reaction failed. A liquid reaction product was obtained from which only o,o'-bitolyl was isolated.

Alkylation of malonic ester with  $\alpha,\alpha'$ -dibromo-3,3'-dichloro-o,o'-bitolyl to cause ring closure proceeded satisfactorily by adapting the procedure used by Iffland and Siegel (14) with the related  $\alpha,\alpha'$ -dibromo-2,2'-bitolyl. Extending this procedure to the  $\alpha,\alpha'$ -dibromo-3,3'-diiodo-o,o'-bitolyl resulted in only a 16% yield of ring closure product in the first reaction attempted, using 0.01 mole of the dibromide. This product provided satisfactory elemental analysis for diethyl 4,8-diiodo-5,7-dihydrodibenzo [a,c] cycloheptene-6,6-dicarboxylate (m.p. 53-55°). Repetition of the reaction with 0.017 mole of the bromide resulted in zero yield of the previously isolated cyclized product (XV). Instead, there was isolated a higher melting product (m.p. 224-225°). Elemental analysis of this material gave carbon and hydrogen per cent values somewhat lower than but near values required for  $\beta,\beta,\beta'\beta'$ -tetracarboethoxy-3,3'-diiodo-2,2'-diethylbiphenyl (XXII).



XXII

The low yield of the desired product in this reaction and the isolation of material which is possibly a mixture containing compound XV suggested that ring closure with the 3,3'-diiodo compound is more difficult than with the 3,3'-dichloro compound. This difference may well be a consequence of greater molecular rigidity in the product with 3,3'-diiodo substituents and, in turn, related to the buttressing effect under investigation.

Accordingly, a third attempt was made in which the mole ratio of malonic ester to the  $\alpha, \alpha'$ -dibromide was reduced from the previous value of two to one. In this case, with slow addition of the malonic ester salt to the dibromide, a 35% yield of the desired cyclized product (XV) was obtained. This control of the reaction with change in reactant ratio parallels

the observation reported by Beaven and coworkers (6), using malonic ester and  $\alpha, \alpha'$ -dibromo-*o,o'*-bitolyl.

It was demonstrated by Iffland and Siegel (14) that diethyl 5,7-dihydro [a,c] cycloheptene-6,6-dicarboxylate (I) was non-planar as evidenced by observed optical activity. The observed facile racemization and the "250 m $\mu$ " biphenyl absorption band are reasonable only if the twist angle between the benzene rings is small.

The ultraviolet spectra of the diethyl 4,8-dichloro-5,7-dihydrodibenzo [a,c] cycloheptene-6,6-dicarboxylate (XIV) prepared in this study was found to be almost identical to that of compound I as shown in Fig. II. It is concluded that the configuration of this biphenyl derivative (XIV) is very similar to that of compound I. In this case, buttressing effect resulting from the chlorine atoms in compound XIV is either negligible or absent, and the stereochemical properties of XIV would be anticipated to be very similar to that reported for compound I.

This conclusion is surprising in view of difference in interference radii of the hydrogen and chlorine atoms, 0.9  $\text{\AA}$  and 1.89  $\text{\AA}$ , respectively (24).

The ultraviolet spectra of the diethyl 4,8-diiodo-5,7-dihydrodibenzo [a,c] cycloheptene-6,6-dicarboxylate (XV) was strikingly different from that of the unsubstituted compound I, or the 4,8-dichloro compound (XIV). No absorption maximum was observed in the 250 m $\mu$  region and a pronounced shoulder appeared at 230 m $\mu$ .

The 230 m $\mu$  shoulder is believed to be a consequence of absorption by the iodine atoms and corresponds to the observed absorption of 3,3'-diiodo-o,o'-bitolyl in the 230 m $\mu$  region (see Fig. I) rather than a shift of the biphenyl band to the shorter wavelength. Absorption in this region is not evident in the spectra of the 3,3'-dichloro-o,o'-bitolyl. Correlation of an absorption band at 230 m $\mu$  with iodine has been observed by others. (4,7).

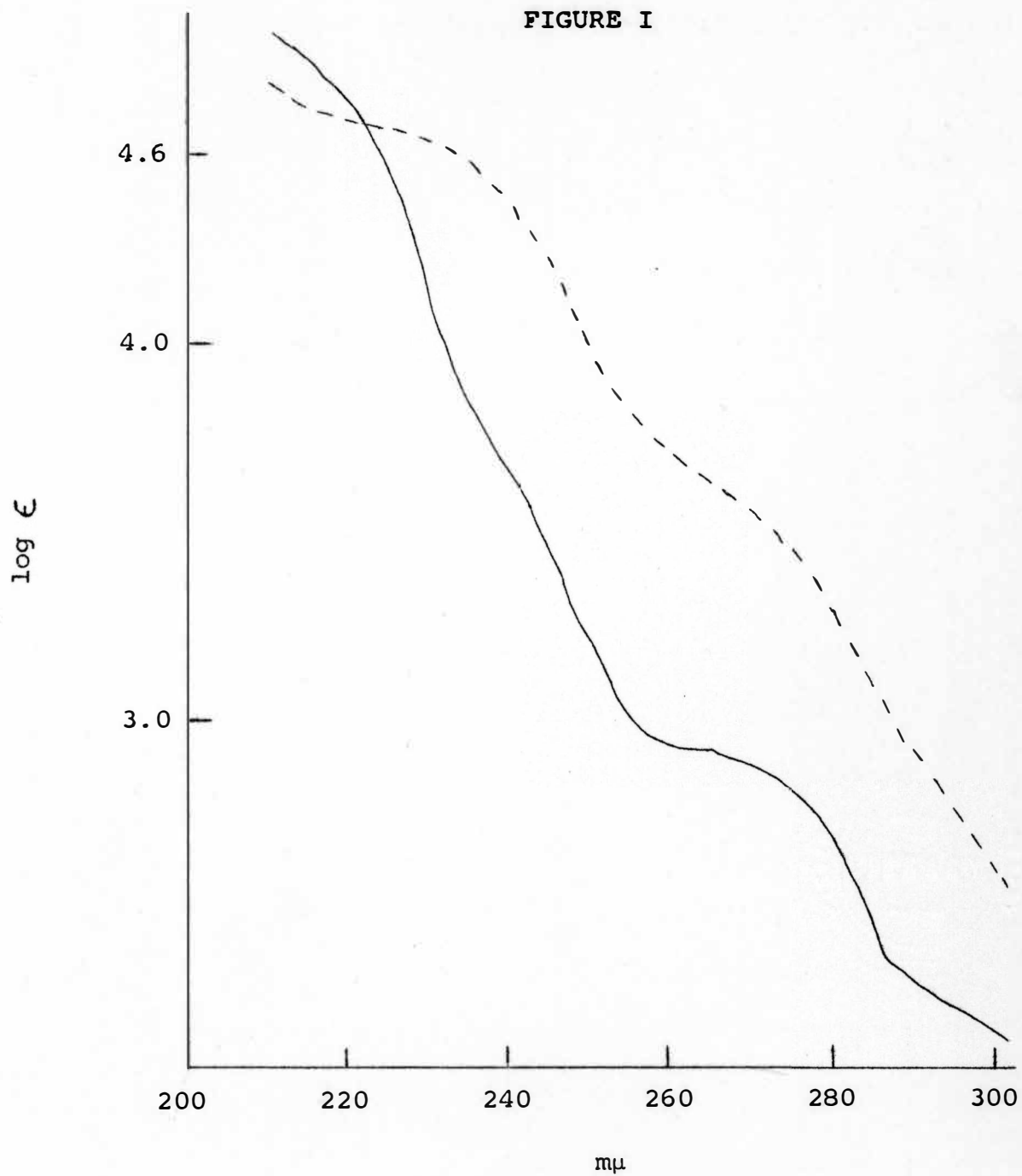
The spectra of the 4,8-diiodo compound (XV) is understandable if the principle molecular conformations have large twist angles between the benzene rings and thus reduce inter-ring conjugation. This is the expected consequence of the buttressing effect of the large substituents in the 4,8-positions (interference radii of iodine is 2.20  $\overset{\text{O}}{\text{\AA}}$ ) (24). Thus, this is the first evidence establishing the existence of buttressing

effect in 3,3'-disubstituted-2,2'-three-atom-bridged biphenyl compounds. These results also establish that the inter-ring conjugation, as indicated by ultraviolet spectra, is eliminated at a twist angle less than that permitted by a 2,2'-three-carbon-atom bridge. Furthermore, this change in conjugation must occur between the twist angle limits present in the 4,8-dichloro (XIV) and the 4,8-diiodo (XV) compounds. Careful examination of scale molecular models may permit an evaluation of these angular limits.

It is now reasonable to expect greater optical stability in the enantiomorphs of the 3,3'-diiodo-2,2'-three-atom-bridged biphenyls. A direct resolution may be a practical method of obtaining the active enantiomorphs rather than an indirect synthesis from optically active intermediates. The 3,3'-dibromo derivatives should be an interesting compound having properties between those observed for XIV and XV.



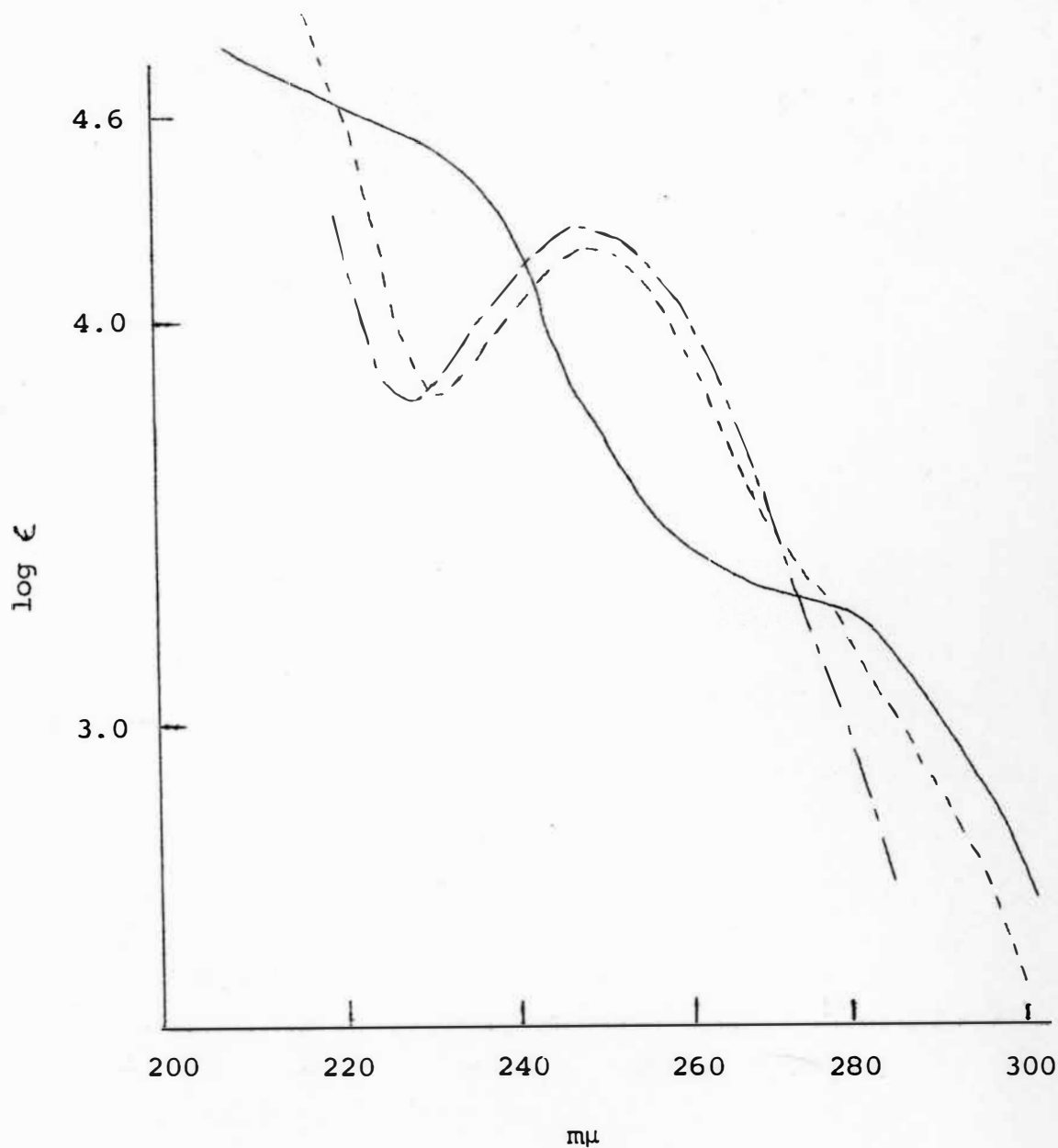
FIGURE I



————— 3,3'-dichloro-2,2'-bitolyl

- - - - - 3,3'-diiodo-2,2'-bitolyl

FIGURE II



- - - - - Diethyl 4,8-dichloro-5,7-dihydrodibenzo  
 [a,c] cycloheptene-6,6-dicarboxylate  
 ————— Diethyl 4,8-diiodo-5,7-dihydrodibenzo  
 [a,c] cycloheptene-6,6-dicarboxylate  
 - - - - - Diethyl 5,7-dihydrodibenzo<sup>[a,c]</sup>cyclohep-  
 tene-6,6-dicarboxylate (14)

## SUMMARY

The diethyl 4,8-dichloro-(XIV) and diethyl 4,8-diiodo-5,7-dihydrodibenzo [a,c] cycloheptene-6,6-dicarboxylate (XV) were prepared. The ultraviolet absorption spectra of compound XIV is similar to 5,7-dihydrodibenzo [a,c] cycloheptene-6,6-dicarboxylate, I, and shows the maximum absorption at 250 m $\mu$  region. It is concluded that the buttressing effect from 4,8-substituents is either negligible or absent. However, the absorption spectra of compound XV has pronounced differences from the spectra of compounds I and XIV. In addition to a shoulder at 230 m $\mu$  resulting from absorption by the iodine atoms, there is no maximum related to inter-ring conjugation. The disappearance of 250 m $\mu$  band was interpreted as proving the existence of the buttressing effect from 4,8-substituents.

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## VITA

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