Resonance in Substituted Biphenyls[1a]
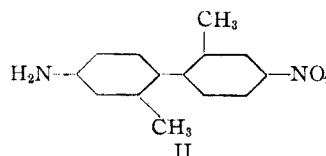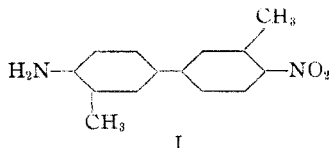
By D. W. SHERWOOD AND M. CALVIN[1b]

As a result of an examination of the optical stability of certain substituted biphenyls, it was suggested[1c] that the shortening of the 1–1' bond of the biphenyl nucleus resulting from resonance of the type
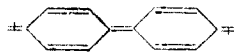
might be held responsible for the resolvability of certain biphenyls having only two ortho substituents. Further, it was pointed out that in the 4-amino-4'-nitrobiphenyl, in which the resonance involving the formation of a 1–1' double bond is greatly enhanced,[2] the interference caused by two ortho substituents should be correspondingly greater. Furthermore, the double bond character of the 1–1' bond might be sufficiently great to introduce a restriction of rotation so as to make possible the distinction of cis and trans isomers about it. Similar substitutions producing a corresponding effect in the opposite direction, i. e., reduction of resistance to rotation about a double bond, have been described for stilbenes.[3]

This paper is the report of an attempt to observe the above effects from a study of the absorption spectra of the corresponding compounds. The relations between absorption spectra, interference, and the existence of isomers have already been described elsewhere.[1c,4,5] In the course of the work it was also possible to measure the base strength of the amino compounds.

The compounds selected as most likely to exhibit these effects are 3,3'-dimethyl-4-amino-4'-nitrobiphenyl (I) and 2,2'-dimethyl-4-amino-4'-nitrobiphenyl (II).

I

(1a) Abstracted from the thesis submitted by D. W. Sherwood in partial fulfillment of the Ph.D. requirements.

(1b) Shell Fellow for 1941–1942.

(1c) M. Calvin, J. Org. Chem., **4**, 256 (1939).

(2) Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, pp. 150, 173.

(3) M. Calvin and R. E. Buckles, THIS JOURNAL, **62**, 3324 (1940).

(4) G. N. Lewis and M. Calvin, Chem. Rev., **25**, 303 (1939).

(5) (a) M. T. O'Shaughnessy and W. H. Rodebush, THIS JOURNAL, **62**, 2906 (1940); (b) B. Williamson and W. H. Rodebush, ibid., **63**, 3018 (1941).

II

The existence of cis and trans isomers of I should make itself apparent in the absorption spectrum provided the spectra of the two forms are sufficiently different and the free energies sufficiently alike. In II the shortening of the 1–1' bond should be easily recognizable through the disappearance of the band due mainly to the amino–nitro resonance through the biphenyl nucleus. In order to properly interpret the spectra of I and II it was necessary to prepare and measure a series of four other compounds as well. These are 4-amino-4'-nitrobiphenyl (III), 3,3'-dimethyl-4,4'-dinitrobiphenyl (IV), 2,2'-dimethyl-4-4'-dinitrobiphenyl (V), 4,4'-dinitrobiphenyl (VI).[5c]

Experimental

4,4'-Dinitrobiphenyl.—This compound was prepared according to the method of Ullmann and Bielecki[6]; yield, 40%, m. p. 236.0–236.5° (cor.). Anal. Calcd.: N, 11.5. Found: N, 11.4, 11.5.

4-Amino-4'-nitrobiphenyl.—4,4'-Dinitrobiphenyl was partially reduced with sodium polysulfide solution by the method of Schultz.[7] It was found that a more pure product resulted from the following procedure: 12.2 g. (0.05 mole) of 4,4'-dinitrobiphenyl was dissolved in boiling ethyl alcohol. About 4 g. of sulfur was dissolved in 120 cc. of 1.25 M sodium sulfide solution while warm, and this polysulfide solution was added dropwise to the alcoholic solution. After boiling for a few minutes, the mixture was evaporated to dryness on the steam-bath. The residue was boiled with 100 ml. of water. After cooling this was filtered and the filtrate containing the inorganic salts was discarded. The residue was extracted with hot 20% aqueous hydrochloric acid. On cooling light yellow crystals deposited. These were shaken with an excess of aqueous ammonia in the presence of a 50–50 mixture of toluene and benzene. The organic solvent layer was then separated and filtered. When concentrated, it yielded good orange crystals, m. p., 203.5°–204.0° (cor.); yield, 35%. Anal. Calcd.: N, 13.1. Found: N, 13.1, 13.0.

3,3'-Dimethyl-4,4'-dinitrobiphenyl.—Preparation was achieved by the nitration of 3,3'-dimethylbiphenyl.[8] The

(5c) During the course of this work the absorption spectrum of 4,4'-dinitrobiphenyl (VI) was published by Williamson and Rodebush.[5b]

(6) Ullmann and Bielecki, Ber., **34**, 2177 (1901).

(7) Schultz, Rohde and Vicari, Ann., **352**, 121 (1907).

(8) Schultz, Rohde and Vicari, Ber., **37**, 1401 (1904); also Ann., **352**, 119 (1907).

3,3'-dimethylbiphenyl was previously prepared by the deamination of o-tolidine according to the method of Mai.[9] The distilling range was 280–282°; yield, 50%. Anal. Calcd.: N, 10.3. Found: N, 10.4, 10.7.

This compound was also prepared by replacing the amino groups of o-tolidine by nitro groups by a modification of the method of Hantzsch and Blagden,[10] with somewhat smaller yields. To a solution of 25 cc. of concentrated sulfuric acid in 200 cc. of water was added 21.2 g. (0.1 mole) of o-tolidine. After heating and stirring, the mixture was cooled to 5–10°, and an aqueous solution of 13.8 g. of sodium nitrite was added dropwise. The cold solution was stirred for two hours and then filtered. The filtrate was mixed with a cold solution of 310 g. of sodium nitrite, and 16 g. of copper powder stirred in. Stirring and gas evolution continued for some time. When the reaction was completed, the mixture was filtered, and the brown residue washed with sulfuric acid.

After trying many solvents, it was found best to boil the residue with glycerol and filter through glass wool to remove the granular red contaminant. The filtrate deposited a feathery yellow material and was diluted with water to make separation possible. The yellow residue was dissolved in alcohol treated with Nuchar, and recrystallized from alcohol twice; m. p. 228.0–228.5° (cor.); yield 25%. Anal. Calcd.: N, 10.3. Found: N, 10.3, 10.4.

3,3'-Dimethyl-4-amino-4'-nitrophenyl.—This compound was prepared from the 3,3'-dimethyl-4,4'-dinitrobiphenyl by the same process as was used for the 4-amino-4'-nitrobiphenyl. It appeared as yellow-orange crystals; m. p. 142.0–142.5°; yield 28%. Anal. Calcd.: N, 11.6. Found: N, 11.5, 11.7.

2,2'-Dimethyl-4,4'-dinitrobiphenyl.—The method was that of Atkinson and Lawler[11] involving the coupling of diazotized amines: 15.2 g. (0.1 mole) of 5-nitro-2-amino toluene was added slowly to 36 cc. of 36 N sulfuric acid and then the mixture cooled to 0°. Over a period of thirty minutes 6.90 g. (0.1 mole) of sodium nitrite was added, and stirring at 0° was continued for four hours. The mixture was then poured onto ice, stirred another hour, and finally filtered. Into a one-liter, three-necked flask was put 49.5 g. (0.495 mole) of pure cuprous chloride, 130 cc. of 13–15 N ammonium hydroxide and 225 cc. of water. Keeping the reducing solution at 25–30°, the diazo solution was slowly added in a period of one and one-half to two hours. Next, the mixture was slowly acidified with 12 N hydrochloric acid, completely dissolving the hydroxides. Filtering yielded an orange residue which was extracted with hot ethyl alcohol, and the extract treated with animal charcoal. On repeated recrystallizations from alcohol light yellow crystals were obtained; m. p. 170°; yield 31%. Anal. Calcd.: N, 10.3. Found: N, 10.3, 10.4.

2,2'-Dimethyl-4-amino-4'-nitrobiphenyl.—The same method was used as for the other aminonitrobiphenyls with the exception that the substance appeared as an oil from toluene and benzene solutions. This oil was extracted with large amounts of hot water, yielding yellow crystals; m. p. 80–81°; yield 21%. Anal. Calcd.: N, 11.56. Found: N, 11.55, 11.50.

(9) Mai, Ber., **35**, 162 (1902).
(10) Hantzsch and Blagden, ibid., **33**, 2553 (1900).
(11) Atkinson and Lawler, THIS JOURNAL, **62**, 1704 (1940).

Absorption Measurements.—The complete absorption spectra were determined by means of a Hilger quartz prism spectrograph. This apparatus has already been described.[3]

In the region of wave length greater than 3000 Å. a Beckmann photoelectric spectrophotometer was used for both the free bases and all of the acid solutions.
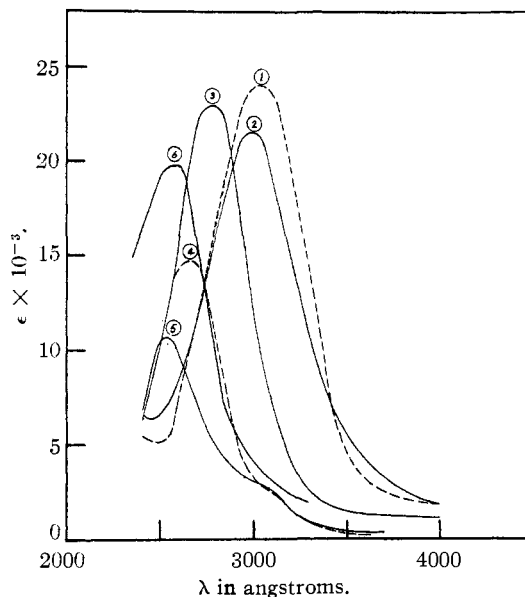

Fig. 1.—
1, 4,4-Dinitrobiphenyl
2, 3,3'-Dimethyl-4,4'-dinitrobiphenyl } 5 × 10^{-5} M in alcohol
3, 2,2'-Dimethyl-4,4'-dinitrobiphenyl
4, m-Nitrotoluene
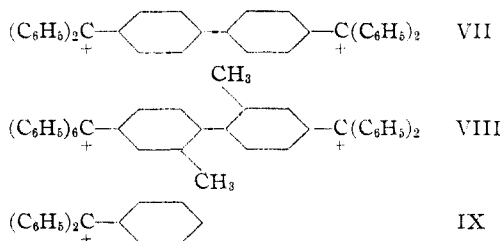5, o-Nitrotoluene } ε × 2
6, Nitrobenzene

Results and Discussion

In Fig. 1 are given the absorption spectra of the three dinitrobiphenyls IV, V, and VI, together with plots of the absorption spectra of the corresponding benzene derivatives with the extinction coefficients multiplied by two. The first thing that is apparent is that in all three biphenyls the resonance between phenyl groups is strong. The effect of a methyl group ortho to a nitro group is, however, much less in the biphenyl than it is in the benzene; compare nitrobenzene and o-nitrotoluene with VI and IV. Although the spatial overlapping of the ortho methyl and the ring-coplanar nitro group must be the same in both compounds (o-nitrotoluene and IV) the actual displacement of the nitro group from coplanarity is less because of the greater resonance interaction of nitro with biphenyl over what it is with phenyl. In compound V, apparently the two methyl–hydrogen repulsions for the trans form, or the methyl–

methyl plus hydrogen–hydrogen interaction for the *cis* form, is insufficient to prevent the resonance between phenyls to any large extent, as is evidenced by the relatively small shift to shorter wave lengths and small decrease in intensity of the band for IV as compared with that of VI. An exactly analogous phenomenon has been observed by Theilacker and Ozegowski[12] in the case of the three ions

$$(C_6H_5)_2C\overset{+}{-}\text{<}\underset{}{\text{=}}\text{>}\text{--}\text{<}\underset{}{\text{=}}\text{>}\overset{+}{-}C(C_6H_5)_2 \quad \text{VII}$$

CH₃

$$(C_6H_5)_6C\overset{+}{-}\text{<}\text{>}\text{--}\text{<}\text{>}\overset{+}{-}C(C_6H_5)_2 \quad \text{VIII}$$

CH₃

$$(C_6H_5)_2C\overset{+}{-}\text{<}\text{>} \quad \text{IX}$$

The 2- and 2′-methyl groups here also are insufficient to completely prevent coplanarity in the absence of any very marked 1–1′ bond shortening. It should be pointed out, however, that in 2,2′-dimethylbiphenyl the resonance band is practically completely eliminated.[5a] This is the same effect as has already been noted in the case of the ortho-methyl–nitro interference and can be attributed to the same causes. When, however, the resonance between phenyls becomes very strong and there tends to be a considerable shortening of the 1–1′ bond (probably somewhat more than 0.1 Å.) the pair of 2,2′-methyls become sufficient to block the main interaction between phenyls.
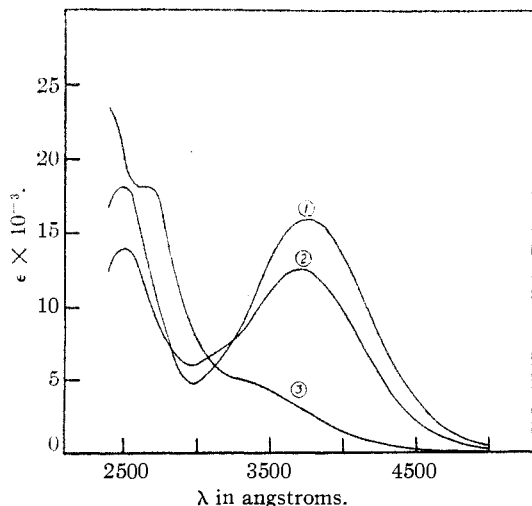

Fig. 2.—1, 4-Amino-4′-nitrobiphenyl, 5×10^{-5} M in alcohol; 2, 3,3′-dimethyl-4-amino-4′-nitrobiphenyl, 10^{-4} M in alcohol; 3, 2,2′-dimethyl-4-amino-4′-nitrobiphenyl, 10^{-4} M in alcohol.

(12) W. Theilacker and W. Ozegowski, *Ber.*, **73**, 898 (1940).

This is exhibited in the next experiments to be described.

In Fig. 2 are shown the absorption spectra of the three amino-nitrobiphenyls I, II, and III. Here again the small effect of the ortho-methyl–nitro interference is apparent. On the other hand, the introduction of the 2,2′ methyls as in II almost completely obliterates the main resonance band in contrast to the small effect of the same substitution as in V. This is to be attributed to the very rapid shortening of the 1–1′ bond as the two approach coplanarity in 4,4′-aminonitrobiphenyls. A similar effect is to be found in the case of the radical forms of VII, VIII, and IX.[12] In this case, where the tendency toward double bond formation in the 1–1′ position is very great, the two 2,2′-methyl groups are sufficient to prevent any great degree of coplanarity.

The question of whether or not there is sufficient double bond character in the 1–1′ bond of I to produce a hindered rotation about this axis and make the existence of recognizable *cis* and *trans* forms possible is not yet answered. The absorption spectrum at room temperature of I shows no evidence of two distinct forms having different absorption bands. This may be due to either or both of two causes. The absorption of the two forms may be so nearly alike that even though they may both be present in appreciable quantities, their broad absorption bands would be indistinguishable. The other possibility is that one form may be sufficiently more stable than the other that an equilibrium mixture of the two would have in it no noticeable quantity of one of the forms. It is hardly to be expected that the resistance to rotation would be so great as to make possible the preparation of a non-equilibrium mixture. Absorption measurements at low temperatures are required to answer this question.

The Acid Strengths of the Amine Salts.—In Figs. 3, 4, and 5 are given the absorption spectra of the aminonitrobiphenyls in solutions of various acid concentrations. It is seen that the main resonance band is gradually diminished as the acidity of the solution increases. This is due to the removal of the basic electron pair of the nitrogen atom from the resonance system by the addition of a proton to form the salt ion. In each case the spectrum for the highest acid concentration shown can be taken to be that of the pure salt ion since further addition of acid does not appreciably change the curve. By assuming that the inter-
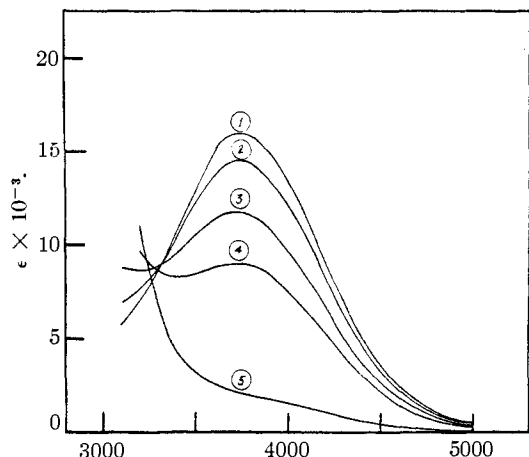
Fig. 3.—4-Amino-4'-nitrobiphenyl in alcoholic hydrogen chloride: 1, free base 5 × 10⁻⁵ M; 2, acid 10⁻⁴ M, base 5 × 10⁻⁵ M; 3, acid 5 × 10⁻⁴ M, base 5 × 10⁻⁵ M; 4, acid 10⁻³ M, base 5 × 10⁻⁵ M; 5, acid 10⁻² M, base 5 × 10⁻⁵ M.
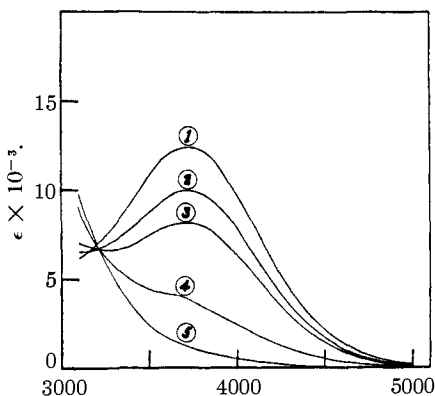

Fig. 4.—3,3'-Dimethyl-4-amino-4'-nitrobiphenyl in alcoholic hydrogen chloride: 1, free base 10⁻⁴ M; 2, acid 2 × 10⁻⁴ M, base 10⁻⁴ M; 3, acid 5 × 10⁻⁴ M, base 10⁻⁴ M; 4, acid 10⁻³ M. base 10⁻⁴ M; 5. acid 10⁻² M, base 10⁻⁴ M.

mediate spectra are the sum of those of the base and salt present in equilibrium it is possible to calculate the amounts of free base and salt present at any acid concentration from the equation

$$\epsilon_{apparent} = \epsilon_B f_B + \epsilon_{BH^+} f_{BH^+}$$

where ϵ is the molar extinction coefficient at some chosen wave length and f is the fraction of the biphenyl in the corresponding form. From these values at various acid concentrations and at vari-
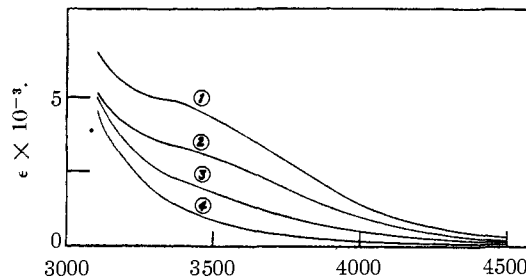

Fig. 5.—2,2'-Dimethyl-4-amino-4'-nitrobiphenyl in alcoholic hydrogen chloride: 1, free base, 10⁻⁴ M; 2, acid 2 × 10⁻⁴ M, base 10⁻⁴ M; 3, acid 10⁻³ M, base 10⁻⁴ M; 4. acid 10⁻² M, base 10⁻⁴ M.

ous wave lengths it is possible to calculate an acid strength equilibrium constant $K = [B][H^+]/[BH^+]$ for each biphenyl with the averaged results as follows: 4-amino-4'-nitrobiphenyl, $K = 10.0 \pm 1 \times 10^{-4}$, 3,3'-dimethyl-4-amino-4'-nitrobiphenyl, $K = 8.5 \pm 1 \times 10^{-4}$, and 2,2'-dimethyl-4-amino-4'-nitrobiphenyl, $K = 3.0 \pm 0.5 \times 10^{-4}$. The parallel between the acid strengths and the absorption spectra is evident. The 3,3'-methyl groups have a relatively small effect on the acid strength whereas the 2,2' methyl groups have a rather large effect. The sources of these effects are the same: i. e., mainly the blocking of the nitro–amino resonance through the forced noncoplanar condition of the molecule.[13]

Summary

1.   The absorption spectra of six substituted biphenyls have been obtained.

2.   An interpretation of these spectra is given in which the shortening of the 1–1' bond by the enhancement of certain resonance contributors in biphenyl seems established. The question of the restriction of rotation about a formal single bond through double-bonded resonance forms is discussed.

3.   The acid strengths of three biphenyl ammonium salts have been measured and their relation to structure and spectra pointed out.

(13) A more detailed discussion of these fairly well established steric effects on acid strength can be found in Chap. VI, "The Theory of Organic Chemistry," by Branch and Calvin, Prentice-Hall. New York. N. Y., 1941.