Studies on the Derivatives of Biphenylene Oxide. VI.
4-Nitrobiphenylene Oxide and its Derivatives.

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In the previous communication⁽¹⁾, it was shown by the present author that the mononitrobiphenylene oxide melting at about 91–93° (uncorr.), which was obtained from the nitration products of biphenylene oxide by fractional distillation and fractional crystallization, should be 4-nitrobiphenylene oxide, not being 1-nitrobiphenylene oxide. This conclusion, however, was nothing but an assumption based upon the tendency of substitution of the hydrogen atoms of biphenylene oxide by the nitro group, because till that time 1-nitrobiphenylene oxide had not yet been prepared by anyone. In the recent investigation⁽²⁾ 1-nitrobiphenylene oxide was prepared, and lately a pure mononitrobiphenylene oxide melting at 126–126.5° (corr.) was isolated by the same author from the above-mentioned fraction melting at 91–93°, by means of repeated recrystallization from glacial acetic acid for the removal of contaminated 2- and 3-nitrobiphenylene oxides. This newly isolated nitro compound was ascertained to be 4-nitrobiphenylene oxide by the depression of its melting point then occurred when mixed with 1-, 2- or 3-nitrobiphenylene oxide. Judging from the yields of 2-nitro (71%), 3-nitro (10%), 4-nitro (crude product, 5%; purified product, 1%) and 1-nitro (none was isolated) compounds, the tendency of the introduction of the nitro group in the formation of the mononitrobiphenylene oxides must be in the order of the positions $2>3>4>1$.

Amido-, acetamido-, dinitro-, trinitro-, tetranitro-, and bromonitrobiphenylene oxides were derived from 4-nitrobiphenylene oxide in confirmation of the last compound. The constitutons of those derivatives were determined, and then the physical properties and the absorption spectra of the four mononitrobiphenylene oxides and their corresponding derivatives were compared one another as in Tables 1–7 and Figs. 1–5 respectively, which will be utilized for the benefit of isolation and identification of those compounds.

The compounds obtained newly by the present author are asterisked in the above tables. Of those compounds, 6-bromo-1-nitro-, 6-bromo-3-nitro- and 6-bromo-4-nitro-biphenylene oxides were prepared from the corresponding nitro compounds by bromination in glacial acetic acid, and 4,6-dinitro-, 2,4,6-trinitro-, and 2,4,6,7-tetranitro-biphenylene oxides, from 4-nitrobiphenylene oxide by successive nitrations. The constitution of those new compounds were established as follows.

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(1) S. Yamashiro, *J. Chem. Soc. Japan*, **57** (1936), 715.

(2) S. Yamashiro, *ibid.*, **59** (1938), 950.

Comparison of the physical properties.

Table 1. Mononitrobiphenylene oxides.

Compound	M.p.(corr.)	Crystal (Crystallizing solvent)	Solubility (e: easily soluble, m: moderately soluble, d: difficultly soluble; e>m>d.)									
			Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Methanol	Ethanol	Actone	Acetic acid	Ethyl acetate
1-Nitro	138 -139°	Pale yellow needle (Ethanol)	d	e	e	e	e	m	m	e	m	e
2-Nitro	186 -186.5°	Pale yellow needle (Acetic acid)	d	d	m	m	m	d	d	m	m	m
3-Nitro	158.5-159.5°	Pale yellow needle (Ethanol)	d	d	m	e	e	m	m	e	m	e
*4-Nitro	126 -126.5°	Pale yellow needle (Acetic acid)	m	e	e	e	e	m	m	e	m	e

Table 2. Amidobiphenylene oxides.

1-Amido	118 -119°	Colourless needle (Ethanol)	e	e	e	e	e	e	e	e	e	e
2-Amido	99°	Colourless needle (Ethanol-water)	d	e	e	e	e	e	e	e	e	e
3-Amido	125 -125.5°	Colourless needle (Ethanol-water)	m	e	e	e	e	e	e	e	e	e
*4-Amido	113.5-114.5°	Colourless needle (Ligroin)	m	e	e	e	e	e	e	e	e	e

Table 3. Acetamidobiphenylene oxides.

1-Acetamido	235 -236°	Colourless short needle (Ethanol-water)	d	d	e	e	e	e	e	e	e	e
2-Acetamido	182°	Colourless needle (Ethanol-water)	d	e	m	e	e	e	e	e	e	e
3-Acetamido	166 -166.5°	Colourless needle (Ethanol)	d	d	m	m	m	m	m	e	e	e
*4-Acetamido	259 -260°	Colourless long needle (Ethanol)	d	d	d	e	m	m	m	e	m	e

Table 4. Dinitrobiphenylene oxides.

Compound	M.p. (corr)	Crystal (Crystallizing solvent)	Solubility (e: easily soluble, m: moderately soluble, d: difficultly soluble; e>m>d.)									
			Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Methanol	Ethanol	Actone	Acetic acid	Ethyl acetate
1,6-Dinitro	263 -264°	Colourless needle (Acetic acid)	d	d	d	m	m	d	d	m	m	m
2,6-Dinitro	255 -256°	Pale yellow needle (Benzene)	d	d	d	m	m	d	d	m	m	m
3,6-Dinitro	329 -330°	Colourless needle (Acetone)	d	d	d	m	m	d	d	m	m	m
*4,6-Dinitro	241 -242°	Colourless needle (Acetic acid)	d	d	d	e	m	d	d	m	m	m
1,8-Dinitro	351 -352°	Pale yellow needle (Ethanol)	d	d	d	d	d	d	d	d	d	d
2,7-Dinitro	326 -327°	Colourless needle (Acetic acid)	d	d	d	d	d	d	d	d	d	d

Table 5. Trinitrobiphenylene oxides.

1,3,6-Trinitro	312 -313°	Small colourless rhombic plate (Benzene)	d	d	d	d	m	d	d	m	m	m
1,3,8-Trinitro	260 -261°	Pale yellow hexagonal plate (Acetone-ethanol)	d	d	d	e	e	d	d	e	e	e
2,3,6-Trinitro	237 -238°	Pale yellow hexagonal plate (Benzene)	d	d	d	d	m	d	d	e	m	e
2,3,7-Trinitro	276.5-277.5°	Pale yellow needle (Benzene)	d	d	d	e	m	d	d	e	e	e
*2,4,6-Trinitro	207 -208°	Pale yellow needle (Ethanol)	d	d	d	e	e	m	m	e	e	e

Table 6. Tetranitrobiphenylene oxides.

Compound	M.p. (corr.)	Crystal (Crystallizing solvent)	Solubility (e: easily soluble, m: moderately soluble, d: difficultly soluble; e>m>d.)									
			Ligroin	Ether	Carbon tetra-chloride	Chloro-form	Benzene	Methanol	Ethanol	Acetone	Acetic acid	Ethyl acetate
1,3,6,8-Tetranitro	262 -263°	Colourless prism (Acetic acid)	d	d	d	d	m	d	d	e	m	e
1,3,6,7-Tetranitro	249 -250°	Colourless needle (Benzene)	d	d	d	d	m	m	m	e	e	e
2,3,6,7-Tetranitro	285 -286°	Colourless needle (Benzene)	d	d	d	d	m	d	d	e	m	e
*2,4,6,7-Tetranitro	253 -254°	Colourless rectangular plate (Benzene)	d	d	d	d	m	d	d	e	m	m

Table 7. Bromonitrobiphenylene oxides.

6-Bromo-1-nitro	231 -232°	Small colourless needle (Carbon tetrachloride)	d	d	m	e	e	d	m	e	m	e
6-Bromo-2-nitro	258 -259°	Colourless needle (Acetic acid)	d	d	m	m	m	d	d	m	m	m
*6-Bromo-3-nitro	226 -227°	Colourless rhombic plate (Acetone)	d	d	m	e	e	d	d	m	m	m
*6-Bromo-4-nitro	189.5-190.5°	Yellow long needle (Acetic acid)	m	e	e	e	e	m	m	e	m	e

The bromination of biphenylene oxide in glacial acetic acid takes place, as shown in Part V⁽³⁾, smoothly at the position 3, not at 1, 2, and 4. This directive action in one phenylene residue of biphenylene oxide must be strengthened by the introduction of a negative nitro group in the other phenylene residue. On the other hand, the bromination of mononitro- and dinitro-biphenylene oxides were examined by the author to be found that no bromine atom can be introduced smoothly into the phenylene residue, in which a nitro group is present. That is to say, the mononitro compounds gave only monobromo derivatives in good yield, whereas the dinitro compounds which have each of the nitro groups in both phenylene residues of a molecule, as in 1,8-, 2,6-, 2,7-, and 3,6-dinitro compounds, gave no bromo derivatives. From those experimental results, it can be concluded that the bromination of x-nitrobiphenylene oxide (x=1, 2, 3, or 4) gives 6-bromo-x-nitrobiphenylene oxide as a main product. A support of this view can be found in the paper communicated by H. Gilman and his co-workers⁽⁴⁾, who had obtained 6-bromo-2-nitrobiphenylene oxide from 2-nitrobiphenylene oxide.

The dinitrobiphenylene oxide derived from 4-nitrobiphenylene oxide must have each of the nitro groups in both phenylene residues separately, forming 4,6-dinitrobiphenylene oxide, because this dinitro compound gave no bromo derivative by bromination. Among the positions (2, 3, and 7) which are free and more active to be taken in the nitration of the 4-6-dinitro compound, 2 and 3 are more favourable than 7 for the introduction of the third nitro group owing to the meta-directive influence of the nitro groups already present in the molecule, because either of the nitro groups of 4,6-dinitrobiphenylene oxide exerts a favourable directipe influence to the position 2 or 3, while neither of them exerts a similar influence to the position 7. Of the positions 2 and 3 again, the former is more favourable than the latter for the introduction of the third nitro group, as in the case of nitration of biphenylene oxide, even if the directive influence of the nitro group at the position 4 causing the nitration at the position 2 is equal to that of the nitro group at the position 6 which causes the nitration at 3. From these considerations, it can be concluded that the trinitro compound obtained from 4,6-dnitrobiphenylene oxide is 2,4,6-trinitrobiphenylene oxide. The tetranitro compound obtained as a main product from the last compound must be 2,4,6,7-tetranitrobiphenylene oxide (along with it 2,4,6,8-tetranitrobiphenylene oxide may be formed, by the bye), because it gave no higher polynitro compound, as in the case of nitration of 1,3,6,8-, 1,3,6,7-, and 2,3,6,7-tetranitrobiphenylene oxides, even when it was heated for a long time with a large excess of fuming nitric acid (d 1.52). On the contrary, if the tetranitro compound were 2,3,4,6-tetranitro-biphenylene oxide, it would give 2,3,4,6,7- and 2,3,4,6,8-pentanitrobiphenylene oxides, as in the case of nitration of 1,3,6- and 2,3,6-trinitrobiphenylene oxides⁽⁵⁾, the former of which gave 1,3,6,7- and 1,3,6,8-tetranitro compounds and the latter, 2,3,6,7- and 2,3,6,8-tetranitro

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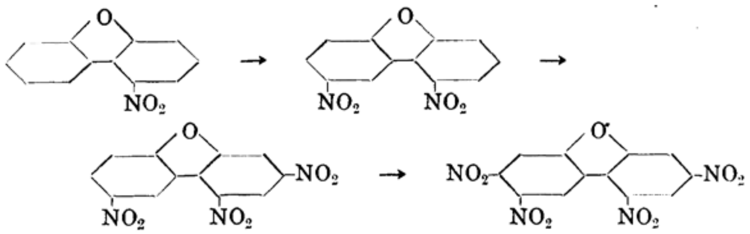
(3) S. Yamashiro, this Bulletin, **15** (1941), 6.

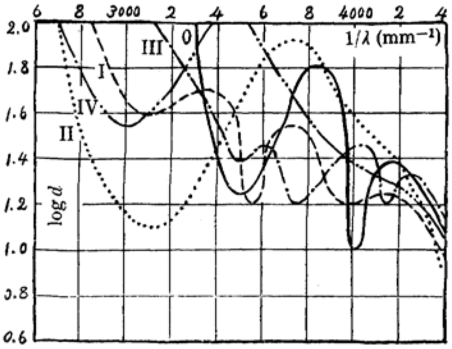
(4) H. Gilman, G. E. Brown, W. B. Bywater and W. H. Kirkpatrick, *J. Am. Chem. Soc.*, **56** (1934), 2476.

(5) S. Yamashiro, *J. Chem. Soc. Japan*, **59** (1938), 448, 450.

compounds. Judging from the reasoning given above, the main reactions of the successive nitrations of 4-nitrobiphenylene oxide may proceed as follows:

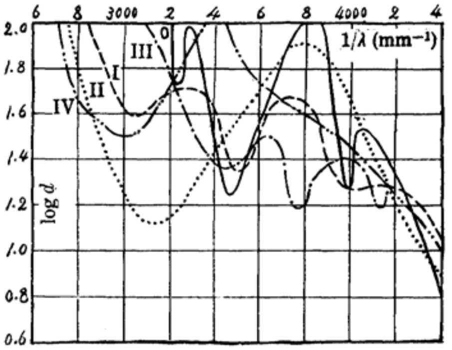


Comparison of the absorption curves.



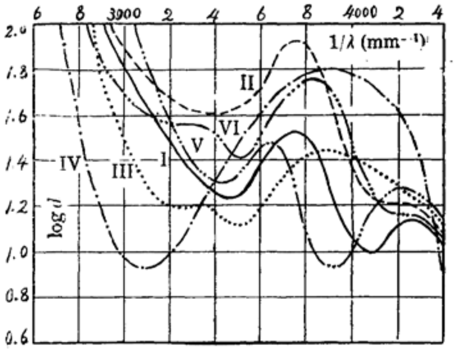
0 (——) Biphenylene oxide.
I (– – –) 1-Nitrobiphenylene oxide.
II (····) 2- ,, ,, .
III (–·–) 3- ,, ,, .
IV (–···–) 4- ,, ,, .

Fig. 1. Mononitrobiphenylene oxides.
M/10000 alcoholic solutions.



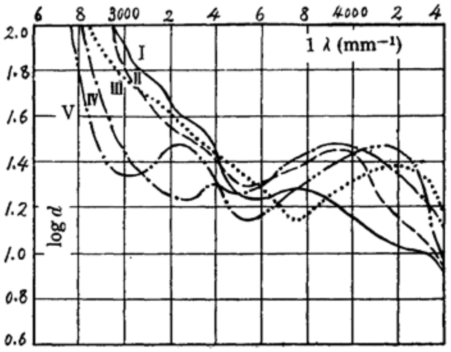
0 (——) 3-Bromobiphenylene oxide.
I (– – –) 6-Bromo-1-nitrobiphenylene oxide.
II (····) 6- ,, -2- ,, ,, .
III (–·–) 6- ,, -3- ,, ,, .
IV (–···–) 6- ,, -4- ,, ,, .

Fig. 2. Bromonitrobiphenylene oxides.
M/10000 alcoholic solutions.



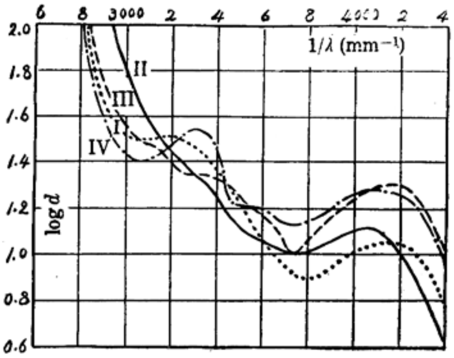
I (——) 1,6-Dinitrobiphenylene oxide.
II (– – –) 1,8- ,, ,, .
III (····) 2,6- ,, ,, .
IV (–·–) 2,7- ,, ,, .
V (–···–) 3,6- ,, ,, .
VI (–····–) 4,6- ,, ,, .

Fig. 3. Dinitrobiphenylene oxides.
M/10000 alcoholic solutions.



I (——) 1,3,6-Trinitrobiphenylene oxide.
II (– – –) 1,3,8- ,, ,, .
III (····) 2,3,6- ,, ,, .
IV (–·–) 2,3,7- ,, ,, .
V (–···–) 2,4,6- ,, ,, .

Fig. 4. Trinitrobiphenylene oxides.
M/10000 alcoholic solutions.



I (——) 1,3,6,7-Tetranitrobiphenylene oxide.
II (– – –) 1,3,6,8- ,, ,, .
III (····) 2,3,6,7- ,, ,, .
IV (–·–) 2,4,6,7- ,, ,, .

Fig. 5. Tetranitrobiphenylene oxides. M/10000.

Among the mononitrobiphenylene oxides, the 1- and 3-nitro compounds having a nitro group at the *o*- and *p*-positions respectively to the ring-forming oxygen atom of biphenylene oxide give two resembling absorption curves, which have three characteristic absorption bands in each other (Fig. 1, Curves I and III), whereas the 2- and 4-nitro compounds, which have both a nitro group at the *m*-position to the ring-forming oxygen atom, give also two resembling curves which have both only one wide characteristic absorption band respectively (Fig. 1, Curves II and IV). The absorption bands of the 1- and 4-nitro compounds are more bathochromic than the corresponding bands of the 3- and 2-nitro isomerides.

As seen from the comparison between the absorption curve of the *x*-nitrobiphenylene oxide ($x=1$, 2, 3 or 4) and that of the corresponding 6-bromo-*x*-nitro compound (Fig. 1, Curves I–IV and Fig. 2, Curves I–IV), the introduction of a bromine atom into the position 6 of the *x*-nitro compound exerts no remarkable influence upon the absorption spectrum of the parent compound.

Similarity of the absorption curves can be found also in the case of dinitrobiphenylene oxides, namely, among the 1,6-, 1,8-, and 3,6-dinitro compounds on one hand (the compounds having nitro groups at the *o,p′*-, *o,o′*- and *p,p′*-positions respectively to the ring-forming oxygen atom; Fig. 3, Curves I, II, and V), and between the 2,6-, and 4,6-dinitro compounds on the other (the compounds substituted at the *m,p′*-positions to the ring-forming oxygen atom; Fig. 3, Curves III and VI). But the 2,7-dinitro compound (the *m,m′*-substituted compound; Fig. 3, Curve IV) gives a curve of special type which is analogous to that of 2-nitrobiphenylene oxide.

In the curves of the trinitro- and tetranitro-biphenylene oxides, no analogy can be found among them, except for those of the 2,4,6-trinitro and 2,4,6,7-tetranitro compounds, both of which give a characteristic absorption band at about $1/\lambda$ (mm^{-1}) 3000, owing to the presence of a nitro group at the position 4 of them.

Experimental.

4-Nitrobiphenylene oxide. As shown in Part I,⁽¹⁾ the reaction products obtained by treating biphenylene oxide (100 g.) with fuming nitric acid (d 1.52; 300 c.c.) in glacial acetic acid (100 c.c.) were recrystallized from acetic acid, when 2-nitrobiphenylene oxide (Yield 71%) was isolated. The mother-liquor was diluted with water precipitating the other components which were fractionated by repeated crystallizations from alcohol and by fractional distillations under the reduced pressure. The fraction distilled out at about the temperature 180–185°/3 mm was again recrystallized from alcohol, when 3-nitrobiphenylene oxide was isolated (Yield 10%). Next, the fraction distilled out up to the temperature 180°/3 mm was repeatedly recrystallized from glacial acetic acid, pale yellow needles melting at 126–126.5° (corr.) (Yield 1%. Found : N, 6.64. Calc. for $C_{12}H_7ONO_2$: N, 6.57%). The last compound is 4-nitrobiphenylene oxide.

4-*Amidobiphenylene oxide.* 4-Nitrobiphenylene oxide (2 g.) was reduced by heating it with stannous chloride (8 g.) and concentrated hydrochloric acid (40 c.c.) in alcohol (300 c.c.). The reaction mixture was evaporated, diluted with water and made strongly alkaline with caustic soda solution precipitating the reduced substance. The base thus separated out was dried quickly, extracted with benzene and the extract was evaporated to dryness. The residue was then recrystallized from ligroin, colourless needles, m.p. 113.5–114.5° (corr.) (Yield 1.86 g., 97.5%. Found : N, 7.70. Calc. for $C_{12}H_7ONH_2$:N, 7.69%.).

4-*Acetamidobiphenylene oxide.* 4-Amidobiphenylene oxide (1 g.) was warmed for a short time with a mixture of acetic anhydride (1 c.c.) and acetic acid (5 c.c.), and then diluted with water precipitating the reaction product, which was recrystallized from alcohol, colourless needless, m.p. 259–260° (corr.) (Yield 1.2 g., 97.6%. Found : N, 6.32. Calc. for $C_{12}H_7ONHCOCH_3$: N, 6.23%.).

6-*Bromo-1-nitrobiphenylene oxide.* 1-Nitrobiphenylene oxide (1 g.) was heated for 5 hours with a large excess of bromine (3. g.) in boiling glacial acetic acid (30 c.c.). After dilution with water, the reaction product separated out was recrystallized from alcohol, colourless needles, m.p. 231–232° (corr.) (Yield 1.28 g., 93.4%. Found : N, 4.81; Br, 27.34. Calc. for $C_{12}H_6OBrNO_2$: N, 4.79; Br, 27.36%.).

6-*Bromo-2-nitrobiphenylene oxide.* 2-Nitrobiphenylene oxide (1 g.) was brominated by the method described by H. Gilman and his co-workers(3) and the reaction product was recrystallized from glacial acetic acid, colourless needles, m.p. 258–259° (corr.) (Yield 1.15 g., 84%. Found:N, 4.82; Br, 27.30. Calc. for $C_{12}H_6OBrNO_2$:N, 4.79; Br, 27.36%.).

6-*Bromo-3-nitrobiphenylene oxide.* 3-Nitrobiphenylene oxide (1 g.) was brominated as in the case of bromination of 1-nitrobiphenylene oxide and the reaction product was recrystallized from acetone, colourless rhombic plates, m.p. 226–227° (corr.) (Yield 1.33 g., 97%. Found:N, 4.86. Br, 27.29. Calc. for $C_{12}H_6OBrNO_2$:N, 4.79; Br, 27.36%.).

6-*Bromo-4-nitrobiphenylene oxide.* 4-Nitrobiphenylene oxide (1 g.) was also brominated as in the case of bromination of 1-nitrobiphenylene oxide and the reaction product obtained was recrystallized from glacial acetic acid, long yellow needles, m.p. 189.5–190.5° (corr.) (Yield 1.20 g., 87.5%. Found : N, 4.84; Br, 27.41. Calc. for $C_{12}H_6OBrNO_2$: N, 4.79; Br, 27.36%.).

4,6(or 3,5)-*Dinitrobiphenylene oxide.* 4-Nitrobiphenylene oxide (2.13 g.) was treated with fuming nitric acid (d 1.45; 20 c.c.) at the room temperature. After 20 minutes, the reaction mixture was poured into water and the reaction product thus separated out (2.5 g.) was recrystallized from glacial acetic acid, colourless needles, m.p. 241–242° (corr.) (Yield 1.70 g., 66%. Found : N, 10.71. Calc. for $C_{12}H_6O(NO_2)_2$: N, 10.85%.). This compound gave no brominated product even when it was heated for a long time with a large excess of bromine in boiling acetic acid.

2,4,6-*Trinitro- and 2,4,6,7-tetranitro-biphenylene oxides.* 4,6-Dinitrobiphenylene oxide (1.29 g.) was heated for 30 minutes with fuming nitric acid (d 1.52; 13 c.c.) and then diluted with water, separating out white precipitates. The reaction products were filtered, dried (Yield 1.58 g.) and extracted with chloroform. The residue was recrystallized from benzene, colourless rectangular plates, m.p. 253–254° (corr.) (Yield 0.196 g., 15.2%. Found : N, 16.12. Calc. for $C_{12}H_4O(NO_2)_4$:N, 16.10%.). The chloroform extract was evaporated to dryness and, after being extracted with 1% hot caustic soda solution to remove the contaminated tetranitro compound, the residue was recrystallized from acetone-alcohol, pale yellow needles, m.p. 207–208° (corr.) (Yield 0.294 g., 22.8%. Found : N, 13.93. Calc. for $C_{12}H_5O(NO_2)_3$: N, 13.87%.). The last trinitro compound was heated for 3 hours with a large excess of fuming nitric acid (d 1.52), when the foregoing tetranitro compound was obtained, but none of the pentanitro compound was isolated. The trinitro and tetranitro compounds obtained here are, as is made clear by the reasoning given above, 2,4,6-trinitro- and 2,4,6,7,-tetranitrobiphenylene oxides respectively.

Summary.

(1) 4-Nitrobiphenylene oxide was isolated in a pure state from the nitration products of biphenylene oxide and the amido, acetamido, dinitro, trinitro, tetranitro and bromonitro derivatives were prepared from it. The constitutions of the latter four derivatives were established.

(2) The physical properties, especially the absorption spectra, of those newly obtained compounds and the corresponding compounds derived from 1-, 2- and 3-nitrobiphenylene oxides were comparatively studied.

In conclusion, the author wishes to express his hearty thanks to Prof. R. Majima of the Osaka Imperial University and Shigemi Oba, the principal of the Yonezawa Higher Technical School, for their kind advices and encouragements. A part of the expense of this investigation has been defrayed from the grant of the Nippon Gakujutsu Shinko-kwai (the Japan Society for the Promotion of Scientific Research) for which also the author wishes to record his thanks.

Yonezawa Higher Technical School.