Biphenylenes. Part XV.[1] 3,7-Dimethyl- and 3,7-Dimethoxy-1,5-dinitrobiphenylene

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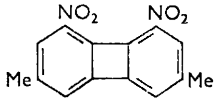
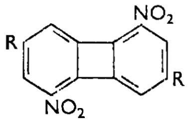
The compound produced by reaction of 3,4-dibromo-5-nitrotoluene with copper bronze has been shown to be 3,7-dimethyl-1,5-dinitrobiphenylene. The analogous 3,7-dimethoxybiphenylene has been prepared similarly from 3,4-dibromo-5-nitroanisole.

The dipole moment of the dimethyldinitrobiphenylene has been found to be about 2·4 D. This unexpected result is discussed.

Recently Corbett and Holt[2] reported that the reaction of 3,4-dibromo-5-nitrotoluene with copper bronze in boiling *NN*-dimethylformamide gave a compound, m. p. 302°, in 40% yield. This compound, $C_{14}H_{10}N_2O_4$, was considered to be either 3,6-dimethyl-1,8-dinitrobiphenylene (I) or the isomeric 3,7-dimethyl-1,5-dinitro-compound (II; R = Me), probably formed by the dimerisation of a benzyne intermediate. We have repeated this reaction, but despite numerous variations of reaction conditions we were unable to obtain more than a 9% yield of the biphenylene, the yield usually being 0—5%.



(I)



(II)

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[1] Part XIV, P. R. Constantine, G. E. Hall, C. R. Harrison, J. F. W. McOmie, and R. J. G. Searle, preceding Paper.

[2] J. F. Corbett and P. F. Holt, *J. Chem. Soc.*, **1961**, **4261**.

The compound, $C_{14}H_{10}N_2O_4$, was reduced by tin and hydrochloric acid to the corresponding diamine. The dihydrochloride of this diamine had an ultraviolet absorption spectrum closely similar to that of 2,6- and 2,7-dimethylbiphenylene, thereby confirming that the dinitro-compound is indeed a biphenylene, since it is known that the electronic absorption spectra of salts of aromatic amines are very similar to those of the parent hydrocarbons.[3,4] The spectra of 2,6- and 2,7-dimethylbiphenylene are too much alike to enable the orientation of the diamine dihydrochloride to be deduced. The diamine dihydrochloride, on treatment with aqueous sodium hydroxide, gave the free diaminodimethylbiphenylene. The n.m.r. spectrum of this compound in trifluoroacetic acid showed a singlet at τ 7·72 (6 protons; two identical methyl groups) and the characteristic pattern for an AB system in the aromatic region (τ 3·15, 3·35; two protons each, $J = 4\cdot5$ c./sec.), showing that there are only two types of aromatic proton and that these are *meta* to each other in each of the benzene rings.

In order to distinguish between structures (I) and (II; R = Me) the dinitrobiphenylene was treated with Raney nickel in ethanol, followed by diazotisation and deamination of the resulting diaminodimethylbiphenyl. The structure of the final product, 3,4′-dimethylbiphenyl, showed that the biphenylene was the 3,7-dimethyl-1,5-dinitro-compound (II; R = Me). This is the orientation which would be expected if its formation proceeded *via* a benzyne intermediate.

Attempts to prepare the isomer (I) by heating 2,2′-dibromo-4,4′-dimethyl-6,6′-dinitrobiphenyl with cuprous oxide alone or with copper bronze in dimethylformamide were unsuccessful. However, the dimethoxybiphenylene (II; R = OMe) was made in 14% yield by heating 3,4-dibromo-5-nitroanisole with copper bronze in dimethylformamide. Its orientation is assumed by analogy with that of the corresponding dimethyl compound (II; R = Me) and from the fact that its ultraviolet spectrum is very similar to that of compound (II; R = Me), allowing for the bathochromic shift caused by replacing the 2,6-dimethyl groups by methoxyl groups, whereas in passing from 2,7-dimethyl- to 2,7-dimethoxy-biphenylene there is a hypsochromic shift of the longer wavelength maxima (cf. Experimental section and ref. 5).

Before the orientation of the compound $C_{14}H_{10}N_2O_4$ had been deduced as described above its dipole moment was measured. Since compounds (I) and (II; R = Me) would be expected to have dipole moments of 7—8 and 0 Debye units respectively this appeared to be a simple way of deciding between the two structures.

The dielectric constants of dilute benzene solutions of dimethyldinitrobiphenylene were measured at 25° by a heterodyne beat method.[6] By assuming linearity of the dielectric constant with the weight fraction w, the mean value of α ($= \delta\varepsilon/\delta w$) was calculated as $2\cdot5 \pm 0\cdot2$. Owing to the limitation of low solubility the variation of specific volume and refractive index with concentration could not be determined accurately. For the latter, however, analogy with the nitrotoluenes and with dimethyldinitrobiphenyls suggested that γ ($= \delta n_D{}^2/\delta w$) should be about 0·2. Thence the orientation polarisation follows[7] as $3M(\alpha - \gamma)v_1/(\varepsilon_1 + 2)^2 = 116\cdot8 \pm 10\cdot2$ c.c. and $\mu = 2\cdot39 \pm 0\cdot13$ D.

This value is difficult to reconcile with the structure of the compound. There is little doubt that its atom polarisation is fairly high and not covered completely by the small allowance made automatically in the method of calculation adopted. This, however, is not likely to exceed greatly the atom polarisation of *p*-dinitrobenzene (~8 c.c.), and in any case should be less than that of 4,4′-dinitrobiphenyl (~22 c.c.). An atom polarisation equal to that of the latter compound, however, would lead to a value for α not greater than 0·6.

An alternative but unlikely explanation, interpreting the high apparent moment as a true permanent moment, would suggest that the axes of the moments of the two nitro-groups must be inclined at about 145° to one another. An allowance of 20 c.c. for atom polarisation leads to a moment of 2·17 D and an angle of inclination of 149° between the moment axes. This could be explained only if the nitro-groups are each bent about 15° out of the plane of the C-9, C-10, C-11, and C-12 atoms.

EXPERIMENTAL

3,7-*Dimethyl*-1,5-*dinitrobiphenylene*.—This was prepared by the method of Corbett and Holt.[2] In the absence of a solvent, no biphenylene was obtained, the product being 2,2′-dibromo-4,4′-dimethyl-6,6′-dinitrobiphenyl (20%). The biphenylene had M (X-ray method), 268 ± 5. Calc. for $C_{14}H_{10}N_2O_4$: M, 270.

1,5-*Diamino*-3,7-*dimethylbiphenylene Dihydrochloride*.—The dinitrobiphenylene (0·25 g.) was dissolved in boiling acetic acid (25 ml.), and concentrated hydrochloric acid (5 ml.) and granulated tin (0·5 g.) were added. After being boiled for 2 hr., the solution was diluted with an equal volume of water and the precipitated solid was recrystallised from very dilute hydrochloric acid, giving the *dihydrochloride* as white needles (0·2 g.) which decomposed above 130° (Found: C, 59·15; H, 5·75; N, 10·1. $C_{14}H_{16}N_2Cl_2$ requires C, 59·35; H, 5·7; N, 9·9%). Light absorption had to be measured in a mixture of ethanol, water, and concentrated hydrochloric acid (25 : 24 : 1 by volume), $\lambda_{max.}$ 246, 255, 341, and 355 mμ (log ε 4·81, 4·95, 3·72, and 3·90). 2,6-Dimethylbiphenylene has $\lambda_{max.}$ (light petroleum) 244, 253, 348, 357, and 368 mμ (log ε 4·71, 4·98, 3·84, 3·67, and 4·03),[8] and 2,7-dimethylbiphenylene has $\lambda_{max.}$ (ethanol) 243, 252, 333 infl., 347, and 365·5 mμ (log ε 4·80, 5·07, 3·51, 3·83, and 3·97).[9]

The dihydrochloride of 1,5-diamino-3,7-dimethylbiphenylene (0·25 g.) was shaken with an excess of 10% sodium hydroxide solution for 30 min. The product was filtered off, washed with water, and recrystallised from

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[3] R. N. Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127.

[4] W. Baker, M. P. V. Boarland, and J. F. W. McOmie, *J. Chem. Soc.*, 1954, 1476.

[5] W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 1958, 2666.

[6] K. Bauge and J. W. Smith, *J. Chem. Soc.*, 1964, 4244.

[7] J. W. Smith, *Trans. Faraday Soc.*, 1950, **46**, 394.

[8] F. A. Hart and F. G. Mann, *J. Chem. Soc.*, 1957, 3939.

[9] Personal communication from G. E. Hall.

methanol to give the free diamine as yellow needles, m. p. 211°.

Degradation of 3,7-*Dimethyl*-1,5-*dinitrobiphenylene to* 3,4′-*Dimethylbiphenyl*.—The biphenylene in ethanol was treated with hydrogen at atmospheric pressure, in presence of Raney nickel, until absorption of hydrogen ceased. The mixture was filtered and the ethanol was removed under reduced pressure. The residue, dissolved in dilute hydrochlorid acid, was treated with aqueous sodium nitrite, and the resulting diazonium salt was reduced by pouring into a ten-fold excess of ice-cold hypophosphorus acid. The mixture was kept at 5° for 3 days and then extracted with ether, yielding 3,4′-dimethylbiphenyl as an oil after distillation at 130°/0·1 mm.

An authentic specimen of 3,4′-dimethylbiphenyl was prepared from 3-bromotoluene and 4-methylcyclohexanone by the method of Hey and Jackson,[10] except that the final aromatisation was carried out with chloranil in boiling xylene.

4-*Amino*-3-*bromo*-5-*nitroanisole*.— Commercial 4-acetamido-3-nitroanisole was deacetylated by boiling with potassium hydroxide in aqueous methanol. The resulting amine (54 g.) was dissolved in acetic acid (200 ml.) and bromine (21 ml.) in acetic acid (50 ml.) was added dropwise, with stirring, at 17°. After 30 min. more, the solution was poured into water and the precipitated *bromo-anisole* was recrystallised from ethanol giving orange needles (55 g.), m. p. 119° (Found: C, 34·3; H, 3·05; N, 11·1. $C_7H_7BrN_2O_3$ requires C, 34·05; H, 2·85; N, 11·35%); τ 1·95 (H_6), 2·21 (H_2) $J_{2,6}$ = 3·3 c./sec.

3,4-*Dibromo*-5-*nitroanisole*.— 4-Amino-3-bromo-5-nitroanisole (40 g.) in acetic acid (100 ml.) was added to an ice-cold solution of sodium nitrite (12·5 g.) in sulphuric acid monohydrate (60 g.). After 30 min. the solution was filtered into an excess of cuprous bromide in 47% hydrobromic acid. After a further 15 min. the solution was heated on a water-bath for 15 min., then diluted with 4 times its volume of water, and the precipitated solid was collected and extracted with ethanol in a Soxhlet apparatus. The extracts yielded the *dibromo-compound* as yellow needles (15 g.), m. p. 98° (Found: C, 27·35; H, 1·7; N, 4·65. $C_7H_5Br_2NO_3$ requires C, 27·05; H, 1·65; N, 4·5%).

3,7-*Dimethoxy*-1,5-*dinitrobiphenylene*.— 3,4-Dibromo-5-nitroanisole (5 g.) and copper bronze (8 g.) in dimethylformamide (75 ml.) were boiled under reflux for 6 hr. The hot solution was filtered and the solids were extracted with more solvent (25 ml.). The combined filtrates, on cooling, gave a solid which was sublimed (140°/0·1 mm.) to give the *dimethoxybiphenylene* (0·35 g., 14%) as orange needles, m. p. 322° after recrystallisation from benzene (Found: C, 55·75; H, 3·45; N, 4·15. $C_{14}H_{10}N_2O_6$ requires C, 55·65; H, 3·35; N, 4·25%); $\lambda_{max.}$ (dioxan) 303 and 454 mμ (log ε 4·07 and 4·01); $\lambda_{max.}$ (acetonitrile) 238, 300, and 451 mμ (peak heights 1·00 : 0·14 : 0·15).

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[10] D. H. Hey and E. R. B. Jackson, *J. Chem. Soc.*, 1934, 648.