The Allegedly Isomeric Diazo-derivatives from " Dehydrothioparatoluidine " (2-p-*Aminophenyl*-6-*methylbenzothiazole*).

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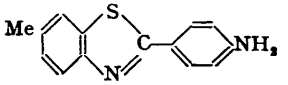
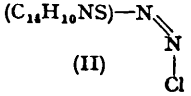
Morgan and Webster's 5-methyl-1-phenylbenzothiazole-4′-*syn*- and -*anti*-diazochlorides are shown to be respectively the diazonium chloride from, and the monohydrochloride of, 2-*p*-aminophenyl-6-methylbenzothiazole. Certain sparingly soluble " diazo-derivatives " of the alleged " *syn*-chloride " should be viewed as diazonium salts with complex anions. Evidence is given that Morgan and Webster prepared an authentic diazocyanide. To date no covalent diazochloride has been isolated, although such structures may be transient intermediates in certain reactions.

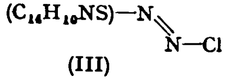
The fact that " dehydrothioparatoluidine " (2-*p*-aminophenyl-6-methylbenzothiazole) (I) could be easily diazotised by sodium nitrite in water to yield " an orange-yellow solution, which is perfectly stable at ordinary temperatures " was originally recorded without further research by Green (*J.*, 1889, **55**, 227). Morgan and Webster (*J.*, 1921, **119**, 1072), however, on repeating the process with ethyl nitrite in absolute alcohol, announced the isolation of isomeric 5-methyl-1-phenylbenzothiazole-*syn*- and -*anti*-4′-diazochlorides (II and III respectively), from which in turn the related diazocyanides and diazosulphonates could be prepared :



(I)



$(C_{14}H_{10}NS){-}N{=}N{-}Cl$ (II)



$(C_{14}H_{10}NS){-}N{=}N{-}Cl$ (III)

Whilst the existence of the last-named derivatives is quite credible (because analogies are well substantiated) that of the chlorides is less so. Two stable chloro-isomers, related as (II) to (III), would be unique in azo-chemistry, where apart from the molecule F·N=N·F (cf. Bauer, *J. Amer. Chem. Soc.*, 1947, **69**, 3104) no instance is known of halogen being covalently joined to the –N:N– unit. Moreover, there are indications that only acids weaker than hydrogen cyanide can produce isolatable diazo-compounds, stronger acids always forming diazonium salts (Saunders, " The Aromatic Diazo-compounds and Their Technical Applications," E. Arnold and Co., 2nd Edn., London, **1949**, p. 388).

For these reasons a re-investigation of the materials described by Morgan and Webster seemed justifiable.

2-p-*Aminophenyl*-6-*methylbenzothiazole and its Diazotisation* (see Morgan and Webster, *loc. cit.*).—The crude powder, recovered from hydrochloric acid extractions of the fusion product, was distilled at atmospheric pressure (b. p. 430—440°) and crystallised from pentyl alcohol, a 31% yield of yellow needles, m. p. 193°, being obtained.

The base (5 g.) in hot ethyl alcohol (80 c.c.) was treated with excess of dry hydrogen chloride to precipitate the salt in a finely divided state. Ethyl nitrite (3 g.) or pentyl nitrite (5 g.) in alcohol was then added slowly with stirring to the mixture held between 0° and 5°. After filtration, the yellow " *syn*-diazochloride " was precipitated from the filtrate by dilution with ether. It had m. p. 139° (decomp.), in agreement with Morgan and Webster, was comparatively stable on a porous tile, and coupled readily with alkaline β-naphthol.

The yellow insoluble residue was extracted successively with boiling chloroform, cold water, and again with chloroform, the extraction with the organic solvent being repeated 14 times. The brownish-yellow amorphous powder thus obtained showed m. p. 269° (decomp.); Morgan and Webster reported 270° (decomp.) for the " *anti*-isomer."

When glacial acetic acid was substituted for alcohol and the pentyl nitrite added at room temperature, a clear solution was obtained (no residue), from which the " *syn*-chloride " could be precipitated by ether. Similar results followed the use of alcohol as medium, and 4 equivs. of hydrochloric acid (*d* 1·16) instead of the gas; with an excess of ethyl nitrite added during 1·5 hr. a clear diazo-solution free from " *anti*-isomer " was again produced.

The Nature of the " syn-Diazochloride."—The substance was insoluble in the common non-polar solvents and dioxan, extremely soluble in water, and much less so in ethyl alcohol, glacial acetic acid, or nitrobenzene.

Comparative observations of the dependence of equivalent conductivity on concentration were made for alcoholic solutions of the "*syn*-chloride," from the amine (I), and of potassium iodide. The conductivity of the " *syn*-chloride " was of the same order as that of the iodide over the concentration range studied (10^{-3}M to 10^{-5}M) and much greater than that of the parent base. This indicated a salt-like character for the " *syn*-chloride," Hantzsch having shown that the electrolytic dissociation of diazonium salt solutions corresponds very closely to that of the analogous potassium and ammonium salts under similar conditions (cf. also Goldschmidt, *Ber.*, 1890, **23**, 3220).

FIG. 1. FIG. 2.

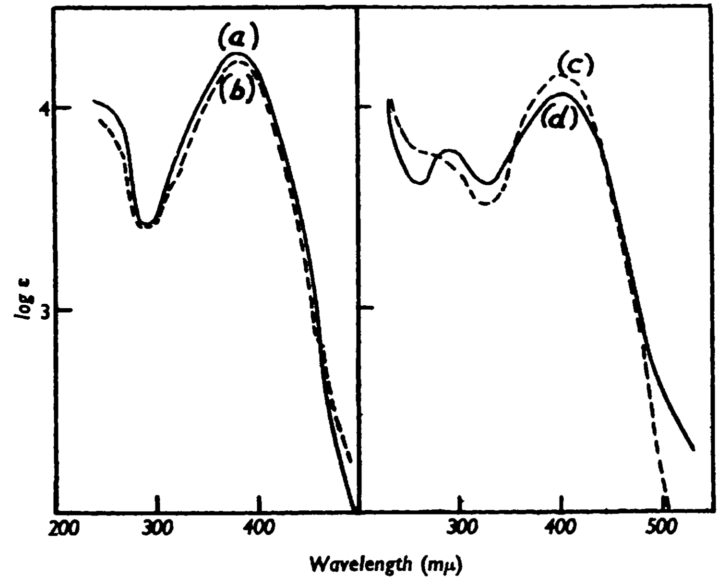


FIG. 1. *Absorption of the " syn-chloride " in* (*a*) *water and* (*b*) *ethanol.*

FIG. 2. *Absorption of the syn-cyanide,* (*c*) *freshly prepared and* (*d*) *after partial conversion into the anti-isomer.*

The " *syn*-chloride " showed practically the same ultraviolet absorption spectrum in water and alcohol (see Fig. 1). Determinations were made with a Beckman Photoelectric Spectrophotometer, model D.U. The solute was freshly precipitated and dried immediately before the solutions were made up; coupling ability was still strong when tested against alkaline β-naphthol at the conclusion of the spectroscopic measurements. The absorption curve is simple, with a single maximum around 390 mμ of an intensity (log ε 4·2—4·3) greater than that usually found for the longer-wavelength band of genuine azo-compounds (*e.g.*, *cis*- or *trans*-azobenzenes, log ε 2·4—3·1 at 430—450 mμ; cf. Le Fèvre and Wilson, *J.*, 1949, 1106); this band apparently replaces the two bands having maxima around 300 and 400—450 mμ which are usual for the –N=N– group (Freeman, Le Fèvre, Northcott, and Worth, *J.*, 1952, 3384) and found for the diazocyanides (see below) corresponding to (II) and (III).

Wohl (*Bull. Soc. chim.*, 1939, **6**, 1319) observed that absorption curves of *ortho*- and *meta*-substituted aryldiazonium chlorides display two maxima, or at least a point of inflexion, but the curves of the related *para*-derivatives have only one branch and a low maximum over the region 220—500 mμ. Since the " *syn*-chloride " is essentially a *para*-substituted aryl compound, its spectrum is therefore not inconsistent with that of a diazonium salt. The immediate relevance, however, of Fig. 1 is to Morgan and Webster's statement that the solubility of the " *syn*-chloride " in water suggests that the diazo-form undergoes a rapid tautomeric change to the diazonium condition: the spectra in water or alcohol indicate that the dissolved species is the same in each solvent; if one accepts that it is a diazonium salt in water, it must be so also in alcohol.

Diazocyanides from the " syn-*Chloride*."—The base (I) (5 g.) was dissolved by heat in the minimum amount of alcohol, then hydrochloric acid (10N; 15 c.c.) was added rapidly with stirring and cooling. The suspension was treated with sodium nitrite (1·5 g.) in water during 1 hr. at 5°. To the filtered diazonium chloride solution, sodium acetate (0·25 g.) and then chloroform (25 c.c.) were added, followed, with vigorous stirring at —10°, by potassium cyanide (in the least amount of water) until the whole was almost but not quite neutral to litmus. The heavy layer after separation and drying (Na_2SO_4) was cooled in carbon dioxide–alcohol, the labile *syn*-diazocyanide separating as a brick-red powder, decomp. 130°. After several hours on a porous tile at room temperature it melted at 175°.

For spectroscopic examination $0{\cdot}3 \times 10^{-4}$M-solutions in sodium-dried ether were made up with newly prepared *syn*-cyanide and kept at 0° in the dark. For each wavelength the observation cell was refilled with fresh solution. On completion of a scan, repetitions at wavelengths used earlier showed insignificant changes, but after the bulk solution had been for 24 hr. in the dark at *ca.* 20° its spectrum was modified as shown in Fig. 2.

Comparison of Fig. 2 with, *e.g.*, Fig. 1 of Le Fèvre and Wilson's paper (*loc. cit.*) reveals a similarity between the *p*-chlorobenzenediazocyanides and the solutes now under examination: two maxima (at *ca.* 300 and 400 mμ) occur in each case, and the effect of storage is to raise the intensity of the band at 300 mμ and to lower that at 400 mμ. These phenomena are consistent with previous experience with *syn*-diazocyanides and their spontaneous (thermal) transformation into *anti*-isomerides (cf. Le Fèvre and Wilson, *loc. cit.*; Freeman and Le Fèvre, *J.*, 1950, 3128; and references cited at end of *J.*, 1949, 1595).

The Nature of the Solid " syn-*Chloride*."—It might be argued that although the " *syn*-chloride " reacts as a diazonium chloride at high dilutions in water or alcohol, it is possibly a covalent diazochloride in the solid state. Accordingly its infrared spectrum as a Nujol mull was recorded over the rock-salt region (Perkin–Elmer 12-C single-beam instrument), four complex compounds being examined at the same time. The latter were obtained by addition of the requisite metallic salt to an aqueous diazotisation solution [prepared from (I) with dilute hydrochloric acid and sodium nitrite], immediate precipitation occurring; these products (see Table) were stable even to drying *in vacuo* over calcium chloride.

5-Methyl-1-phenylbenzothiazole-4′-diazonium salts.

(*a*) Ferrichloride, $(R{\cdot}N_2)^+FeCl_4^-$, m. p. 113° (expln.)
(*b*) Tetrachloroiodide, $(R{\cdot}N_2)^+ICl_4^-$, m. p. 128° (expln.)
(*c*) Zincichloride, $(R{\cdot}N_2)_2^{++}ZnCl_4^{--}$, m. p. 224° (decomp.)
(*d*) Borofluoride, $(R{\cdot}N_2)^+BF_4^-$, m. p. 151° (decomp.)

From their mode of formation they were " stabilised diazonium salts " (cf. Saunders, *op. cit.*, p. 76; Hodgson and Sibbald, *J.*, 1945, 819; Chattaway, Garton, and Parkes, *J.*, 1924, **125**, 1980; Schmidt and Maier, *J. prakt. Chem.*, 1932, **132**, 153; Le Fèvre and Turner, *J.*, 1930, 1158). Bands are sent out in Table 1. Where it has been impossible to differentiate between closely situated absorption bands, assignments are ascribed to the group of frequencies (cf. Randall, Fowler, Fuson, and Dangl, " Infrared Determination of Organic Structures," Van Nostrand, New York, 1949; Ferguson, " Electron Structures of Organic Molecules," Prentice Hall, New York, 1952; Le Fèvre, O'Dwyer, and Werner, *Austral. J. Chem.*, 1953, **6**, 341; Gilman, " Organic Chemistry," Wiley, New York, 1953, Vol. III, Chap. 2; Thompson, *J.*, 1948, 328). The term " strong "(s) indicates an absorption intensity of the order of the strongest bands throughout the given spectrum, " medium " (m) intensities approximately one- to two-thirds of this maximum, and " weak " (w) those lower than one-third.

TABLE 1. *Infrared absorptions (cm.$^{-1}$) of the solid " syn-chloride," etc.*

" *syn*-Chloride "	Salt (*a*)	Salt (*b*)	Salt (*c*)	Salt (*d*)	Assignment
3380 (w)	—	3410 (w)	—	—	
—	3110 (w)	3090 (w)	3080 (m)	3100 (m)	C–H str.
2270 (s)	2264 (s)	2235 (s)	2275 (s)	2290 (s)	$(-N{\equiv}N)^+$
1576 (s)	1579 (s)	1576 (s)	1578 (s)	1582 (s)	Ph and benzothiazole-II
—	1495 (m)	—	—	1497 (m)	Ph and benzothiazole-I
—	1411 (m)	1411 (w)	—	1416 (m)	
—	—	1323 (m)	1323 (m)	—	
1312 (m)	1311 (m)	1311 (m)	1303 (m)	1312 (s)	C–N
—	—	—	1274 (m)	—	
1250 (m)	1256 (m)	1255 (m)	1252 (m)	1263 (m)	*para*-Disubstd. benzene and C–N and 1 : 2 : 4-trisubstd. benzene
1230 (w)	1234 (w)	—	—	1236 (w)	
1218 (w)	1220 (w)	—	—	1223 (w)	
	1205 (w)	1204 (w)	—	—	
1168 (w)	1186 (w)	—	—	1190 (w)	
1132 (w)	—	1132 (w)	—	1124 (m)	
—	—	1114 (w)	—	—	
1077 (m)	1083 (s)	1074 (s)	1075 (m)	1086 (s)	
1058 (w)	1059 (m)	—	—	1064 (s)	
1012 (w)	—	1006 (w)	990 (w)	1028 (s)	
966 (m)	968 (m)	971 (m)	966 (w)	972 (s)	C–N
—	—	885 (w)	—	—	
887 (w)	875 (w)	878 (w)	889 (w)	877 (w)	1 : 2-Disubstd. and 1 : 2 : 4-trisubstd. benzene
845 (s)	838 (s)	846 (s)	—	843 (s)	
—	—	834 (s)	833 (s)	—	
802 (s)	814 (s)	817 (m)	808 (s)	824 (s)	
758 (m)	759 (m)	759 (m)	764 (m)	759 (m)	
708 (w)	707 (w)	—	712 (m)	707 (w)	C–S–C
—	693 (w)	692 (w)	691 (m)	694 (m)	Ar ring

It is seen that each of the five substances absorbs strongly between 2235 and 2290 cm.$^{-1}$, a region in which the base (I) and its hydrochloride are transparent (cf. Table 3). Le Fèvre, Werner, and Aroney (*J.*, **1955**, **276**) have shown 21 diazonium salts to possess a common band between the limits 2231 and 2306 cm.$^{-1}$ (mean, 2261 cm.$^{-1}$) and have attributed this to the $(R-N{\equiv}N)^+$ cation. We conclude therefore that Morgan and Webster's " *syn*-diazochloride " is the diazonium chloride from the benzothiazole (I).

Morgan and Webster's " syn-Complexes."—Morgan and Webster prepared a number of sparingly soluble coloured compounds (by double decomposition of their alleged " *syn*-diazochloride " with soluble metallic salts containing the required anion) which they assumed to belong to the *syn*-series of diazo-structures. Three examples of these have been re-examined: the ferricyanide, the chromate, and the nitroprusside. A calcium fluoride prism of approximate resolving power 2 cm.$^{-1}$ being used, medium-strong absorptions were noted at 2275, 2264, and 2258 cm.$^{-1}$ respectively, from which we infer the presence of the diazonium group. The " *syn*-complexes " must therefore be diazonium salts with complex anions, and Morgan and Webster's " *syn*-diazo "-terminology for them must be rejected.

Other absorptions found within the range 3225—1350 cm.$^{-1}$ are included in Table 2. The

TABLE 2. *Infrared absorptions of " syn-complexes " between 3225 and 1350 cm.$^{-1}$.*

Ferricyanide	Chromate	Nitroprusside	Assignment
3090 (w)	—	3075 (w)	Aromatic C–H str.
2275 (s–m)	2264 (s–m)	2258 (s–m)	$(-N{\equiv}N)^+$
—	—	2131 (w)	(CN)
2107 (m)	—	—	
—	—	1895 (s)	? (NO)
1580 (s)	1579 (m)	1577 (w)	Ph and benzothiazole-I

features assigned as (CN) occur at points between those allotted as the ferrocyanide band at 2075 cm.$^{-1}$ and the ferricyanide band at 2166 cm.$^{-1}$ by Emschwiller (*Compt. rend.*, **1954**, **238**, 1414) when considering the spectrum of Prussian blue. The frequency of the co-ordinated (NO) group is less certain. In $Na_2[Fe(CN)_5NO]$ it appears at 1925 cm.$^{-1}$ (Miller and Wilkins, *Analyt. Chem.*, 1952, **24**, 1253). The benzothiazole base absorbs weakly at 1886 cm.$^{-1}$, and it may be that (NO) absorption superposed on this produces the strong band at 1895 cm.$^{-1}$.

The Nature of the Solid " anti-Chloride."—Electrical-conductivity measurements indicated that the material was dissociated to the same extent as the hydrochloride of the benzothiazole (I). A mild red colour was still obtained with alkaline β-naphthol, even after twenty extractions with chloroform, although no increase of coupling then followed acidification (showing that the "*anti*-chloride" was not an insoluble diazoamino-derivative). Analysis further suggested that the compound was the monohydrochloride of the base (Found: C, 60·8; H, 4·6; N, 9·9. Calc. for $C_{14}H_{13}N_2SCl$: C, 60·9; H, 4·7; N, 10·1%). The m. p. was 269° (decomp.) and, when mixed with authentic hydrochloride [270° (decomp.)], was 269—270° (decomp.). The infrared spectrum of the "*anti*-isomer" showed no band at 2235—2290 cm.$^{-1}$ (and therefore seemed not to be a diazonium salt); in all other major details it resembled the monohydrochloride of (I) of which we conclude it to be a slightly impure sample.

The analytical figures published by Morgan and Webster diverge considerably from those required for the diazochloride and their accuracy is open to doubt. The fact that the "*anti*-isomer" residue is obtained only when diazotisation is carried out in alcohol and not in aqueous mineral acids or glacial acetic acid suggests that diazotisation in alcohol is much slower than in the other solvents and that unused monohydrochloride then remains as insoluble residue. This is supported by the observation that excess of ethyl nitrite and a longer reaction period results in the formation of the diazonium chloride exclusively.

TABLE 3. *Infrared absorptions of the base* (I) *and its hydrochloride.*

Base (I)	Hydrochloride	Assignments
3460 (m)	—	N–H
3298 (m)	—	
3177 (m)	—	
—	2490 (m)	$C–NH_3^+\}Cl^-$
—	2020 (w)	
1886 (w)	—	
1626 (s)	1609 (s)	$Ar–NH_2$; C=N
1602 (s)	1590 (s)	Ph and benzothiazole-I
1568 (m)	—	N–H
—	1495 (s)	Ph and benzothiazole-II; C–N
1305 (s)	1317 (m)	
—	1302 (m)	
1280 (m)	1277 (s)	
1256 (m)	1250 (m)	
1227 (m)	1225 (s)	
1177 (s)	1190 (m)	C–N
—	1148 (s)	
1124 (m)	1128 (m)	*p*-Disubstd. benzene
—	1120 (m)	
1060 (w)	1058 (w)	
1036 (w)	1042 (w)	
1005 (w)	1024 (w)	1 : 2 : 4-Trisubstd. benzene
—	985 (m)	
968 (s)	972 (w)	
—	953 (w)	
—	896 (m)	
887 (w)	887 (m)	C–N
864 (w)	877 (m)	
—	837 (m)	*p*-Disubstd. benzene
—	830 (m)	
822 (s)	824 (m)	
812 (s)	812 (s)	1 : 2 : 4-Trisubstd. benzene
—	803 (m)	
705 (w)	718 (m)	C–S–C
—	711 (w)	
693 (m)	693 (s)	Ar–ring

The Existence of Covalent Diazo-halides.—In the light of the present work it seems that stable covalent diazo-halides have not as yet been isolated. *A priori* there seems little reason for this. Many cases are known where halogen is covalently linked to nitrogen: relevantly it may be noted that geometrically isomeric ketone chloroimines are separable and have had their dipole moments measured (Theilacker and Fauser, *Annalen*, 1939, **539**, 103), that the molecule F·N=N·F is stable and has been examined by electron diffraction (Bauer, *J. Amer. Chem. Soc.*, 1947, **69**, 3104), and that chlorine, bromine, and iodine azides exist (albeit as highly explosive substances). Throughout diazo-chemistry, however, there is much evidence for diazonium–diazo-equilibria, and the possibility has been mooted of diazo-halides' playing a transient part in certain reactions, such as coupling in the presence of pyridine (Hodgson, *J. Soc. Dyers and Colourists*, 1942, **58**, 228) or the reduction of diazonium salts by alcohols (replacement of N_2X by H; Huisgen and Nataken, *Annalen*, 1951, **573**, 181).

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