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An "Ortho Effect" in 2-Arylnaphthotriazole Systems

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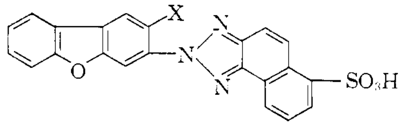
A pronounced "*ortho* effect" was observed in the ultraviolet absorption spectra of a series of 2-(*o*-substituted phenyl)- and 2-(*p*-substituted phenyl)-naphthotriazoles. Every *o*-substituent studied (fluoro, chloro, methoxyl, sulfo and nitro) regardless of size or electronic character, shifted the absorption maximum to shorter wave lengths and sharply reduced the intensity of absorption, as compared with the corresponding *p*-substituent. The magnitude of this "*ortho* effect" is unexpectedly large.

During the study of a variety of triazole systems, an unusual spectral effect, first noted on comparing the ultraviolet absorption spectra of compounds I and II, was observed.

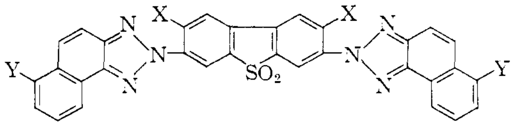


I, X = H
λ_{max} 351 mμ
ϵ_{max} 42,300

II, X = OCH$_3$
λ_{max} 333 mμ
ϵ_{max} 22,800

The introduction of a methoxyl group *ortho* to the junction between the triazole and aryl rings (Compound II) causes a hypochromic effect and hypsochromic shift. Normally, a methoxyl substituent would be expected to produce at least a small bathochromic shift.

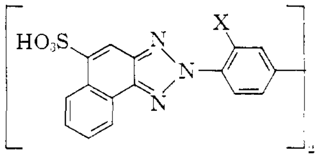
A more pronounced effect was observed in a series of bis-naphthotriazoles (III–VIII).



III, X = H, Y = SO$_3$H; λ_{max} 378 mμ and 397 mμ
ϵ_{max} 76,400 and 75,100

IV, X = SO$_3$H, Y = H; λ_{max} 336 mμ
ϵ_{max} 26,400

V, X = Y = SO$_3$H; λ_{max} 340 mμ
ϵ_{max} 29,300



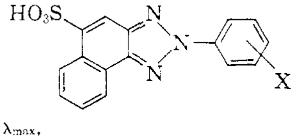
VI, X = H; λ_{max} 366 mμ; ϵ_{max} 79,500
VII, X = Cl; λ_{max} 338 mμ; ϵ_{max} 36,700

To study this effect in its simplest form, a series of simple 2-phenylnaphthotriazoles was prepared and the ultraviolet absorption spectra of the model compounds determined and compared (Table I).

Every substituent studied, fluoro, chloro, methoxyl, nitro and sulfo, regardless of size or electronic character (inductive or conjugative) had a pronounced hypsochromic and hypochromic effect on the absorption spectrum when in the *o*-position, as compared with the corresponding substituent in the *p*-position. Recently, similar observations have been reported by others.[1,2]

TABLE I

ULTRAVIOLET ABSORPTION DATA FOR 2-PHENYLNAPHTHOTRIAZOLES

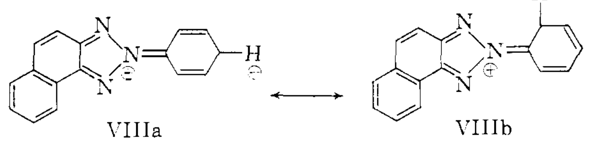


X	λ_{max}, mμ[a]	ϵ_{max}	X	λ_{max}, mμ[a]	ϵ_{max}
H	340	19,300	*p*-Chloro	340	24,100
o-Methoxyl	333	9,600	*o*-Sulfo	332	9,100
p-Methoxyl	345	18,500	*m*-Sulfo	340	21,600
o,*p*-Difluoro	335	13,700	*p*-Sulfo	340	24,100
p-Fluoro	340	19,600	*o*-Nitro	340	13,300
o-Chloro	330	9,400	*p*-Nitro	360	30,400
m-Chloro	340	21,600			

[a] The first absorption band in the near ultraviolet region was selected. There are indications, as evidenced by the appearance of well defined shoulders in several cases, that this band is composed of three individual absorptions which have been smoothed over by the polar medium. The middle absorption band is clearly dominant and is the one cited in the table.

The most important implication of these data is that there is electronic interaction between the phenyl and triazole rings of the type normally requiring coplanarity which is inhibited by the *o*-substituent. Explaining this interaction in terms of currently available valence-bond symbolism presents an intriguing problem; indeed, the correct representation of the triazole system, itself, is a perplexing problem.[3] These two problems are, of course, closely related. Any solution to the general problem must accommodate several facts. First, electron-withdrawing substituents, such as nitro, chloro, fluoro and sulfo, in the *p*-position of the 2-phenylnaphthotriazole system produce derivatives which are hyperchromic with respect to the unsubstituted parent. Weakly electron-releasing groups, such as *p*-methoxyl are, correspondingly, hypochromic.

Dobáš, Pirkl and Hanousek[1a] have proposed a solution to this general problem *via* the model VIII.



VIIIa VIIIb

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(1) J. Dobáš, J. Pirkl and V. Hanousek, *Coll. Czech. Chem. Comm.*, **23**, (1958); (a) 280; (b) 915; (c) 926; (d) 1346; (e) 1357.

(2) V. Chmátal, J. Liskočil and Z. J. Allan, *ibid.*, **24**, 494 (1959).

(3) F. Mužík and Z. J. Allan, *Chem. Listy*, **46**, 350 (1952); *Coll. Czech. Chem. Comm.*, **18**, 388 (1953); *Chem. Listy*, **48**, 221 (1954); *Coll. Czech. Chem. Comm.*, **19**, 953 (1954).

This model is in accord with the data for electron-withdrawing substituents and methoxyl. On the other hand, the model fails to account for the fact that *p*-amino, strongly electron-donating group, is also hyperchromic with respect to the unsubstituted parent.[1d]

Accordingly, we lean to the view that this problem cannot be solved by a classical approach and suggest that a molecular orbital treatment may be more suitable.

Surprisingly, the magnitude of the steric requirement of the 2-phenylnaphthotriazole system is considerably larger than would be predicted from an examination of the steric requirements of other azole systems for which spectral data are available. Thus in the phenylbenzimidazole system an *o*-methoxyl causes a decrease in extinction coefficient of 14% compared with *p*-methoxyl[4]; in the 2,5-diphenyloxazole series, 24%.[5] The corresponding value in the triazole series is 48% (Table I).

o-Chlorine in both the benzimidazole[4] and 2,5-diphenyloxazole series,[5] produces a 45% decrease in extinction coefficient, compared with a 61% reduction in the naphthotriazole system. Fluorine in the 2,5-diphenyloxazole series results in an 8% decrease in extinction coefficient[5]; but the decrease is 30% in the naphthotriazole system.

Another striking comparison is that with the biphenyl series where a single *o*-methoxyl substituent causes a hypsochromic shift of 2 m*u* and reduction in extinction coefficient of 29% as compared with biphenyl. In the 2-phenylnaphthotriazole system, the corresponding values are 7 and 50%. This comparison is surprising if one considers that the 5-membered triazole ring is bent back more sharply than the 6-membered phenyl ring and, further, there are no hydrogen atoms projecting from the triazole ring. On the other hand, the C–N bond is somewhat shorter than the C–C bond (assuming that the same bond-order obtains).

An additional observation is that the magnitude of the effect is not entirely proportional to the size of the substituent. The very small and compact chlorine atom produces as great an effect as the much bulkier sulfonate group. Thus, in addition to bulk, electrostatic repulsions must be an important factor in this "*ortho* effect." This appears to be especially true with *o*-chlorine and *o*-fluorine and would involve the non-bonding electrons on the halogens and ring nitrogens (N_1 and N_3).

Acknowledgment.—Microanalyses were determined by Mr. O. E. Sundberg and associates. The ultraviolet absorption data were supplied by Mr. F. C. Dexter (Beckman DU spectrophotometer; 40% aqueous ethanol, ammonium acetate buffer). The author is indebted to Mr. G. Hooper and Dr. F. Marascia for technical assistance and to Drs. F. Brody and J. J. Leavitt for guidance and encouragement during the course of this study.

Experimental

2-(3-Dibenzofuryl)-2H-naphtho[1,2]triazole-6-sulfonic Acid, Sodium Salt.—The azo dye, prepared by diazotizing 3-aminodibenzofuran and coupling with 2-aminonaphthalene-5-sulfonic acid, was cyclized to the triazole by heating at reflux with copper sulfate (5 molar equivalents) in the presence of a large excess of ammonia for a total period of 7 hours. The solid product which was isolated from the reaction mixture was treated with sodium hydroxide and sodium sulfide and then extracted exhaustively with alcohol. The extract was concentrated to a very small volume. The solid product obtained was recrystallized from methanol including treatment with activated carbon and clarification.

Anal. Calcd. for $C_{22}H_{12}N_3O_4SNa$: C. 60.42; H, 2.76; N, 9.61; S, 7.33. Found: C, 60.3; H, 2.72; N, 9.61; S, 7.57.

2-(2-Methoxy-3-dibenzofuryl)-2H-naphtho[1,2]triazole-6-sulfonic Acid, Sodium Salt (II).—The azo dye, prepared by diazotizing 3-amino-2-methoxydibenzofuran and coupling with 2-aminonaphthalene-5-sulfonic acid, was cyclized as above except that methanol and pyridine were added to the reaction mixture to help solubilize the azo dye. The reaction mixture was not fully decolorized even after 30 hours. The solid product was suspended in 1:1 hydrochloric acid (to leach out the copper) and subsequently extracted with boiling methanol. The extract was made basic to litmus by addition of 5 *N* sodium hydroxide, and a small amount of copper oxide was filtered and discarded. The clear solution was treated with aqueous sodium hypochlorite to discharge the red color and was then concentrated to a very small volume. The product was recrystallized from boiling methanol. The sample was largely the sodium salt of the desired compound contaminated, apparently, with some ammonium salt.

Anal. Calcd. for $C_{23}H_{19}N_3O_5SNa$: C, 59.10; H, 3.02; N, 8.99; S, 6.86. Found: C, 58.2, 58.2; H, 3.00, 3.06; N, 9.70, 9.33; S, 6.81. Reduced Values (98.5%): C, 58.2; H, 2.97; N, 8.87; S, 6.76.

3,7-Bis-(6-sulfo-2H-naphthotriazol-2-yl)-dibenzothiophene 5,5-Dioxide, Sodium Salt (III).—The azo dye, prepared by tetrazotizing 3,7-diaminodibenzothiophene 5,5-dioxide and coupling with two molar equivalents of 2-aminonaphthalene-5-sulfonic acid, was dissolved in a mixture of equal volumes of pyridine, water and ethylene glycol and oxidized with five molar equivalents of ammoniacal copper sulfate. The reaction was complete in about 20 hours. The product was freed from copper by leaching with hot dilute hydrochloric acid and was recrystallized several times from dimethylformamide–methyl alcohol containing sodium hydroxide.

Anal. Calcd. for $C_{32}H_{16}N_6O_8S_3Na_2 \cdot 1/2H_2O$: C, 50.32; H, 2.25; N, 11.01; S, 12.59. Found: C, 50.2; H, 2.49; N, 11.1; S, 12.6.

3,7-Bis-(2H-naphtho[1,2]triazol-2-yl)-dibenzothiophene 5,5-Dioxide-2,8-disulfonic Acid, Sodium Salt (IV).—The azo dye, prepared by tetrazotizing 3,7-diaminodibenzothiophene-5,5-dioxide-2,8-disulfonic acid and coupling with two molar equivalents of 2-aminonaphthalene, was cyclized and purified as described above.

Anal. Calcd. for $C_{32}H_{16}N_6O_8SNa_2 \cdot H_2O \cdot$ C, 46.49; H, 2.92; N, 10.17; S, 11.63. Found: C, 47.1, 46.5; H, 2,52, 2.59; N, 8.31, 8.30; S, 11.6. Calcd. for 92% $C_{32}H_{16}N_6O_8S_3Na_2$: C, 46.8; H, 1.97; N, 10.5; S, 11.8.

3,7-Bis-(6-sulfo-2H-naphtho[1,2]triazol-2-yl)-dibenzothiophene-5,5-dioxide-2,8-disulfonic Acid, Sodium Salt (V).—The azo dye, prepared by tetrazotizing 3,7-diaminodibenzothiophene-5,5-dioxide-2,8-disulfonic acid and coupling with 2 molar equivalents of 2-aminonaphthalene-5-sulfonic acid, was cyclized with 5 molar equivalents of ammoniacal copper sulfate in aqueous medium. The product was recrystallized from ethyl alcohol, containing the smallest amount of water to give a clear solution at the boil.

Anal. Calcd. for $C_{32}H_{14}N_6O_{14}S_5Na_4 \cdot 3H_2O$: C, 37.95; H, 1.99; N, 8.30; S, 15.83. Found: C, 38.0, 37.6; H, 1.98, 2.20; N, 8.79; S, 16.1.

Biphenylene-4,4'-bis-[2-(2H-naphtho(1,2)triazole-5-sulfonic Acid)], Sodium Salt (VI),—The azo dye, congo red, was cyclized with 5 molar equivalents of ammoniacal copper sulfate in a solvent mixture of equal parts of water, pyridine

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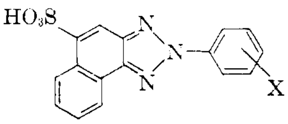
[4] A. Mangini and F. Montanari, *Boll. Sci. fac. chim. ind. Bologna*, **14**, 36 (1956).

[5] D. G. Ott, F. N. Hayes, E. Hansbury and V. N. Kerr, THIS JOURNAL, **79**, 5448 (1957).

TABLE II



X	Composition	Analyses, %							
		Calcd.				Found			
		C	H	N	S	C	H	N	S
H	$C_{16}H_{10}N_3O_3SNa \cdot H_2O$	52.60	3.11	11.51	8.77	52.7, 52.7	3.04, 3.11	11.9	8.80, 8.81
o-OCH_3	$C_{17}H_{12}N_3O_4SNa \cdot H_2O$	51.65 4.56[a]	3.57	10.64	8.11	51.86, 51.92 4.08, 3.80[a]	3.82, 3.96	10.26, 10.30	8.12
p-OCH_3	$C_{17}H_{12}N_3O_4SNa \cdot H_2O$	51.65 4.56[a]	3.57	10.64	8.11	51.82, 51.68 5.64, 5.69[a]	3.53, 3.79	9.89, 10.05	8.25
o-Cl	$C_{16}H_9ClN_3O_3SNa$	50.34 9.29[b]	2.38	11.02	8.40	50.01 8.95[b]	2.11	11.08	8.33
m-Cl	$C_{16}H_9ClN_3SNa \cdot H_2O$	48.07 8.87[b]	2.77	10.51	8.02	48.08, 47.98 9.04[b]	2.72, 2.66	10.82	8.52
p-Cl	$C_{16}H_9ClN_3O_3SNa \cdot H_2O$	48.07 8.87[b]	2.77	10.51	8.02	47.75, 47.93 8.67[b]	2.57, 2.99	10.70	8.42
o-SO_3H	$C_{16}H_9N_3O_6S_2Na_2 \cdot 2H_2O$	39.59	2.70	8.66	13.21	39.9	2.61	8.35, 8.65	13.0
m-SO_3H	$C_{16}H_9N_3O_6S_2Na_2 \cdot {}^1/_2H_2O$	41.92	2.20	9.17	13.99	41.3, 41.6	2.05, 2.09	9.43	14.0
p-SO_3H	$C_{16}H_9N_3O_6S_2Na_2 \cdot H_2O$	41.12	2.37	8.99	13.72	41.3, 41.1	2.62, 2.67	8.83	12.8, 13.2
o,p-F_2	$C_{16}H_8F_2N_3O_3SNa \cdot H_2O$	47.90 4.49[a]	2.51	10.47	7.99	47.84 4.60[a]	2.71	10.59	8.10
p-F	$C_{16}H_9FN_3O_3SNa \cdot 2H_2O$	47.90 8.98[a]	3.27	10.47	7.98	47.76 9.25, 9.08[a]	3.74	10.72	7.68, 7.41
o-NO_2	$C_{16}H_9N_4O_5SNa \cdot H_2O$	46.84 4.39[a]	2.70	13.66	7.81	46.66 3.91, 3.61[a]	2.69	13.56	7.79, 7.63
p-NO_2	$C_{16}H_{10}N_4O_5S \cdot NH_3 \cdot H_2O$	47.40 4.20[c] 4.45[a]	3.73	17.28	7.91	47.16 4.32[c] 4.87, 4.95[a]	3.59	17.11	7.82, 7.79

[a] H_2O. [b] Cl. [c] NH_3.

and ethylene glycol. The product, freed of copper, was recrystallized from dimethylformamide–methanol.

Anal. Calcd. for $C_{32}H_{18}N_6O_6S_2Na_2$: C, 55.49; H, 2.62; N, 12.14; S, 9.26. Found: C, 55.2; H, 2.86; N, 12.1; S, 9.40.

3,3'-Dichloro-4,4'-diphenylene-bis-[2-(2H-naphtho(1,2)-triazole-5-sulfonic Acid)] Sodium Salt (VII).—The azo dye, prepared by tetrazotizing 3,3'-dichlorobenzidine and coupling with 2 molar equivalents of naphthionic acid, was slurried with about 10 parts by volume of dimethylformamide and treated cold with 75 ml. of 13% sodium hypochlorite. The crude product was washed free of inorganic salts.

Anal. Calcd. for $C_{32}H_{16}Cl_2N_6S_2Na_2 \cdot 3H_2O$: C, 47.12; H, 2.72; Cl, 8.69; N, 10.31; S, 7.86. Found: C, 47.4; H, 2.52; Cl, 9.14; N, 10.1, 10.4: S, 7.42. Calcd. for 93.6% $C_{32}H_{16}Cl_2N_6O_6Na_2$: C, 47.4; H, 1.99; Cl, 8.74; N, 10.6; S, 7.90.

Substituted 2-Phenyl-2H-naphtho[1,2]triazoles—Table II.—The azo precursors were cyclized by the normal ammoniacal copper sulfate procedure, employing 5 molar equivalents of copper sulfate and a large excess of ammonia. Reactions were run in aqueous alcohol or aqueous pyridine to promote better solubility.

The products were purified by leaching with dilute hydrochloric acid to remove copper and recrystallization from alcohol or aqueous alcohol.

Determination of the Ultraviolet Spectra.—The samples, sodium or ammonium salts, used for determination of the ultraviolet absorption spectra were those on which the microanalyses had been run. Solutions were made up to contain 10 mg. of sample ("as is" basis) per liter of solution (40% aqueous alcohol, buffered with ammonium acetate).

The value for ϵ_{max} was calculated using the molecular weight of the free acid form of the compound and correcting for the actual free acid content of each sample as indicated by its composition.