

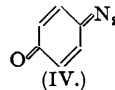
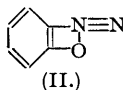
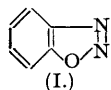
447. Dipole Moment and Spectrographic Data for Certain Diazophenols and Diazonaphthols.

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The dipole moments and ultra-violet spectra of two diazophenols and four diazonaphthols indicate that quinonoid structures contribute predominantly to the real structures, in contrast with benzthiadiazole, for which a covalent cyclic formulation seems satisfactory. Data for "azibenzil" are also included.

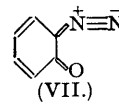
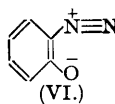
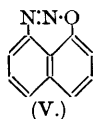
RECENTLY (*Chem. and Ind.*, 1948, 158, 543, 732, 782) reasons were listed for believing that, in certain molecules containing it, the azo-grouping is able to adopt a *cis*-configuration. Similarities between *cis*-azobenzene and benzocinnoline (Calderbank and Le Fèvre, *J.*, 1948, 1949) formed part of the evidence, since in the latter molecule a *cis*-arrangement is fixed by ring formation. Other substances possibly having the same structural feature became, therefore, of obvious relevance, and we accordingly investigated representative members of the classes covered by the title of this paper.

History.—Satisfactory formulations for these compounds have been debated for years. Since they were theoretically derivable from *o*- and *p*- (but not *m*-)amino-phenols or -naphthols containing a similar grouping, earlier investigators assumed *ortho*- or *para*-rings to be involved, e.g., (I) (Bamberger, *Ber.*, 1895, 28, 837; Morgan and Porter, *J.*, 1915, 107, 645) or (II) (Klemenc, *Ber.*, 1914, 47, 1407), although Wolff (*Annalen*, 1900, 312, 119) had favoured quinonoid repre-

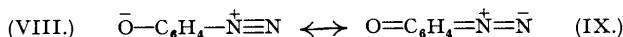


sentations, e.g., (III) or (IV), largely on the argument of colour. Such formulæ have lately received further support from ultra-violet spectroscopy (Anderson and Roedel, *J. Amer. Chem. Soc.*, 1945, 67, 955). The similarities of properties and reactions—indicating a corresponding similarity of structure—between the *ortho*- and the *para*-series, coupled with the stereochemical awkwardness of a 1 : 4-covalent bridge in the latter, strongly suggest that (I) may be disregarded. The position would be different were the *peri*-diazo-oxide (V)—for which a quinonoid skeleton is impossible—known certainly to exist. It has been mentioned in a number of German patents

(cf. Morgan and Micklethwait, *J.*, 1908, **93**, 607), but Anderson and Roedel (*loc. cit.*) specifically report their unsuccessful attempts to repeat its preparation.



Hodgson and Marsden (*J. Soc. Dyers Col.*, 1943, **59**, 271) concluded that all known diazo-oxides can be best regarded as resonance hybrids, *e.g.*, (VI) \longleftrightarrow (VII), or generally:—



Present Work.—The last suggestion is amenable to examination by means of dipole moments. If this hypothesis were correct, it is obvious that observed polarities should considerably exceed the values expected for the fully quinonoid structures such as (VII) or (IX) in proportion as the ionised forms contribute to the real structures. Wyman (*Chem. Reviews*, 1936, **19**, 213) has noted that true "zwitterion" molecules probably have the large moments which their formulæ indicate.

For the present enquiry, therefore, we made the necessary measurements on the substances listed in Table I. In the third and the fourth column we list estimated moments (μ_Q and μ_Z) for the quinonoid and ionised molecules, respectively. These values are necessarily somewhat speculative. Ordinary benzenoid geometry, atomic radii, etc., have been assumed, together with $\mu_{\text{C:O}} = \text{ca. } 3 \text{ D.}$ (cf. acenaphthaquinone or phenanthraquinone, Caldwell and Le Fèvre, *J.*, 1939, 1614), $\mu_{\text{C:N}_2} = \text{ca. } 1.4 \text{ D.}$ (cf. the diaryldiazomethanes, Sidgwick, Sutton, and Thomas, *J.*, 1933, 406), $\mu_{\text{C:NO}_2} = 4 \text{ D.}$, and $\mu_{\text{C:Br}} = 1.5 \text{ D.}$ (cf. the corresponding $\text{C}_6\text{H}_5\cdot\text{X}$ compounds). In the fifth column are shown the solutions to the equation, $\mu_{\text{observed}} = \alpha_Q^2\mu_Q + \alpha_Z^2\mu_Z$ (cf. Sutton, *Trans. Faraday Soc.*, 1934, **30**, 789), where α_Q^2 and α_Z^2 indicate the relative importances of the contributing forms.

TABLE I.

	$\mu_{\text{obs.}}$	μ_Q	μ_Z	α_Q^2	α_Z^2
3 : 5-Dibromo-1 : 2-benzoquinone-2-diazide	2.9	2.5	13.1	1	0
1 : 2-Naphthaquinone-1-diazide	4.0	3.9	13.7	1	0
1 : 2-Naphthaquinone-2-diazide	3.5	3.9	13.7	1	0
4-Nitro-1 : 2-naphthaquinone-1-diazide	4.6	2.8	16.2	0.9	0.1
1 : 4-Naphthaquinonediazide	4.2	1.6	27.4	0.9	0.1
<i>p</i> -Benzoquinonediazide	5.0	1.6	27.4	0.9	0.1

From the data in Table I it appears that contributions from fully dipolar structures are small. A preliminary forecast of this conclusion has already appeared (Anderson and Le Fèvre, *Nature*, 1948, **162**, 449).

In this connection we note the evidence from studies of thermal decomposition (Vaughan and Phillips, *J.*, 1947, 1560), where certain *o*-diazio-oxides appear to be less stable than their *p*-analogues. The differences are explained by a restriction of resonance in the former by the proximity of opposite electrostatic charges, the ionised form thus tending to preponderate, and the resonance energy to have a smaller value, so causing a lessening of stability. At first sight our results seem to indicate, if anything, a situation which contradicts this prediction.

Recognising, however, the uncertainty of the assumptions we have made, we hesitate to conclude from the six examples in Table I that contributions from fully dipolar forms are more marked in the *p*- than in the *o*-series, since we have also found that the parent substance (III) can be isolated only as a hydrate, which has not yet been successfully dehydrated. We have examined (III) spectroscopically in alcoholic solution, but it has proved too sparingly soluble in benzene for measurement of the dielectric constant. It therefore possibly has a high polarity, and would in this way support the theory of Vaughan and Phillips.

While disregarding a formula of type (I) for the *o*-series, we are not unaware that moments of the orders now found, *e.g.*, for the dibromo-derivative, might be expected on its basis. However, in addition to the reason already given (chemical resemblances between 1 : 2- and 1 : 4-members), we may add another, namely, that O- and S-containing heterocyclic analogues usually have a recognisable parallelism in physical properties such as *m. p.*, *b. p.*, colour, solubility, etc. We have accordingly examined benz-1-thia-2 : 3-diazole (I; S substituted for O) which, in contrast to all the substances of Table I, is low-melting, colourless, easily soluble in non-polar solvents, and volatile in steam (*vide* Beilstein, "Handbuch," **27**, 567).

Yet, notwithstanding the complete dissimilarity from the diazo-oxides, its dipole moment (3.5_4 D.) is of their order, and of that to be expected from rough vectorial considerations (cf. Hunter and Partington, *J.*, 1933, 87, *re* $\mu_{\text{O.S.}}$). Hodgson and Marsden (*loc. cit.*) commented on the significance of the apparent non-existence of *p*-diazo-sulphides and drew the conclusions, with which we agree, that the 1:2-sulphides, unlike the oxides, possess a covalent -N=N-X- chain. Such a decision is not novel (cf. Sidgwick, "Organic Chemistry of Nitrogen," Oxford, 1937, p. 422, where incidentally the related triazoles are included with the thiadiazoles). Its interest to us (*vide Chem. and Ind.*, 1948, 158) lies in the fact that, with benzcinnoline, here is another quite stable molecule in which the -N=N- arrangement is *cis*-.

Absorption Spectra.—Various new determinations have been made, using the Beckman photoelectric spectrophotometer, model D.U. They are incorporated with previously recorded data in Tables II, III, and IV. The three groupings used in the above tables are chosen somewhat arbitrarily to show the degree of resemblance between the absorption by related molecules containing >C=N_2 and >C=O . Such a parallelism was first claimed by Wolf (*Z. physikal. Chem.*, 1932, B, 17, 46) for ethyl diazoacetate and certain ketones, although Hantzsch and Lifschitz (*Ber.*, 1912, 45, 3011) had previously used it to decide that *p*-diazophenol was quinonoid in character. Its most extensive application to the present problem has been by Anderson and Roedel (*loc. cit.*). The measurements made with our various products obtained in attempted preparations of the unsubstituted 1:2-benzoquinonediazide (III) are not included in Table III since they were qualitative only. Absorptions were noted as follows:

(a) Ethereal extract from alkaline solution.....	422	300	272	256	242
(b) Ethereal extract from acid solution	416	308	272	255 *	—
(c) Alcoholic solution of solid after partial dehydration to constant weight	403	—	—	263	—

* Inflexion.

A certain similarity with the results of Table II is apparent. Fukushima and Horio (*Mem. Coll. Eng. Kyoto Imp. Univ.*, 1931, 6, 179) have likewise reported semiquantitative spectra for the diazotisation products of *o*-, *m*-, and *p*-aminophenol and 1-amino-2-naphthol-4-sulphonic acid. Their figures for maximum absorption are:

Product from <i>o</i> -aminophenol	392; 345 *; 263.
„ „ <i>p</i> -aminophenol	358 *; 338; 238; 212.*
„ „ aminonaphtholsulphonic acid	393; 327; 286; 247.*

TABLE II.

		<i>Diazides.</i>		
<i>p</i> -Benzoquinonediazide	<i>E</i> ¹	448 * (1.80)	342 (4.47)	287 (3.37)
				279 (3.51)
1:4-Naphthaquinonediazide	<i>E</i> ¹	477 * (1.81)	371 (4.55)	312 (3.83)
				291 (4.00)
				282 (4.00)
				242 (3.73)
3:5-Dibromo-1:2-benzoquinonediazide	<i>H</i> ⁵	—	419 * (3.55)	285 (3.97)
				408 (3.59)
				349 * (3.31)
4-Nitro-1:2-benzoquinone-1-diazide	<i>A</i> ⁵	—	396 (3.79)	258 (4.07)
				325 (4.03)
				238 (4.00)
1:2-Naphthaquinone-1-diazide	<i>E</i> ¹	455 * (2.1)	404 (3.65)	285 (4.21)
				388 (3.78)
				278 * (4.13)
				370 (3.72)
				250 (4.29)
1:2-Naphthaquinone-2-diazide	<i>E</i> ¹	475 * (2.0)	413 * (3.82)	305 (3.80)
				397 (4.00)
				293 (3.80)
				389 * (3.95)
				261 (4.57)
4-Nitro-1:2-naphthaquinone-1-diazide	<i>H</i> ⁵	—	400 * (3.49)	284 (3.90)
				395 (3.51)
				247 (4.16)
				332 (3.35)
Azibenzil	<i>E</i> ^{1, 5}	434 (2.04)	319 (3.73)	264 (4.29)

Inflections are indicated by asterisks, and solvents by *A* = alcohol, *E* = ether, *H* = *n*-hexane in this and other tables.

TABLE III.
Related quinones and benzil.

<i>p</i> -Benzoquinone	<i>H</i> ^{3,4}	478 (1.08)	—	280 (2.57)
		457 (1.29)		242 (4.34)
		434 (1.30)		
"	<i>E</i> ⁴	472 (1.10)	—	278 (2.85)
		455 (1.28)		242 (4.36)
		443 (1.18)		
		429 (1.30)		
		417* (1.13)		
"	<i>A</i> ⁴	412 (1.20)		
		435 (1.28)	—	296 (2.63) 242 (4.25)
1 : 2-Naphthaquinone	<i>E</i> ¹	538 (1.55)	389 (3.55)	252 (4.52)
		503 (1.54)	331 (3.54)	248 (4.50)
1 : 4-	"	424 (1.65)	331 (3.50)	below 250
		403 (1.67)		
Benzil	<i>E</i> ¹	386 (1.83)	335 * (2.22)	273 * (4.1)
		368 (1.81)		259 (4.36)

TABLE IV.
Thiadiazoles and triazoles.

Benz-1-thia-2 : 3-diazole	<i>H</i> ⁵	—	306 (3.63)	264 (3.92) 254 (4.02) 225 (4.23)
Naphtho(1' : 2'-5 : 4)-1 : 2 : 3-thiadiazole	<i>E</i> ¹	—	353 (3.35)	282 * (3.93)
			338 (3.37)	255 (4.76)
Benz-1 : 2 : 3-triazole	<i>A</i> ²	—	291 * (3.32)	282.5 * (3.58) 276 (3.65) 259 (3.58)
Naphtho(1' : 2'-5 : 4)-1 : 2 : 3-triazole	<i>E</i> ¹	ca. 350 * (1.70)	342 (3.81)	283 (4.06)
			316 * (3.42)	272 (4.07)
			312 (3.68)	251 (4.57)
			305 (3.35)	247 (4.60)
		298 (3.37)		

¹ Anderson and Roedel (*loc. cit.*).³ Klingstedt, *Compt. rend.*, 1923, **176**, 1550.⁵ Present work.² Macbeth and Price, *J.*, 1936, 111.⁴ Braude, *J.*, 1945, 490.

They remark on the difference between the data just quoted and those for the product from *m*-aminophenol (compare the non-occurrence of 1 : 3-diazo-oxides).

A propos formula (VI) it is relevant that the spectra of Table II are quite distinct from those of corresponding methoxy-diazonium salts, for which Wohl (*Bull. Soc. chim.*, 1939, **6**, 1319) has found :

<i>o</i> -Sulphate	353 (3.65); 263 (4.05).
<i>p</i> - "	326 (4.10); 311 (4.50); 291 * (4.00); 270 * (3.55); 254 (3.05).

Finally, Tables II and IV, in conjunction, again suggest separate structures for the diazo-oxides and the thiadiazoles, and similar ones for the latter and the triazoles. When S replaces O or NH, the change is generally indicated spectrometrically more by alterations of intensity than of wave-length of maximum absorption. A few examples are collected in Table V. The appearance of extra bands is sometimes notable :

TABLE V.

Oxygen compounds.	Sulphur compounds.	Nitrogen compounds
Et·O·Et ¹ 190 * (3.00)	Et·S·Et ¹ 195 (3.15)	Et·NH·Et ¹ 195 (3.45)
Ph·OH ¹ 275 f. (2.30)	Ph·SH ¹ 269 f. (2.86)	Ph·NH ₂ ¹ 280 f. (2.30)
Furan ^{1,2} 250 (0.00)	Thiophen ^{1,2,3} 268 * (-0.25)	Pyrrole ^{1,2} 240 (2.48)
234 (3.64)		
215 (2.1)		
Oxazole ⁴ 230 (1.48)	Thiazole ¹ 240 (3.60)	Glyoxaline ¹ 250 (1.78.)

¹ Braude, *Ann. Reports*, 1945, **42**, 105.² Godart, *J. Chem. Phys.*, 1937, **34**, 70.³ Menszel, Thesis, Zurich, quoted in (2).⁴ Cornforth and Cornforth, *J.*, 1947, 96.

f. indicates a group of subsidiary maxima.

By analogy, therefore, if the diazo-oxides were structurally related to the thiadiazoles they should not absorb at wave-lengths much greater than 350 μ . In fact, of course, their absorption extends right up to the visible region. By the reverse argument, noting that thioketones often absorb in the red (Braude, *loc. cit.*), the transparency of the thiadiazoles down to 350 μ , strongly suggests that, in them, the C=S group is absent.

EXPERIMENTAL.

Materials.—3:5-Dibromo-1:2-benzoquinone-2-diaziide was prepared (yield, 12%) as stated by Orton (*Proc. Roy. Soc.*, 1903, **71**, 153). It decomposed at 140° after preliminary melting at temperatures which varied with the rate of heating; Orton (*loc. cit.*) and Bamberger and Kraus (*Ber.*, 1906, **39**, 4251) record the same phenomenon.

The isolation of *o*-benzoquinonediaziide was attempted many times. Spectroscopic indications were that it was formed during the diazotisation of *o*-aminophenol, *e.g.*, addition of ether immediately after the sodium nitrite, followed—under vigorous stirring—by aqueous sodium hydroxide during 15 minutes until the whole was alkaline, gave, after drying (Na_2SO_4), the solution whose absorptions have already been mentioned (*a*, p. 2084); further acidification of the aqueous portion with nitric acid and another extraction with ether, etc. afforded the second solution (*b*, p. 2084).

A solid was finally obtained by diazotising, at 5° with amyl nitrite (7 c.c.), *o*-aminophenol (5 g.) in alcohol (80 c.c.) containing hydrogen chloride (5 g.). The diazonium chloride was isolated by precipitation with ether, suspended in amyl alcohol (100 c.c.), and stirred at 0° with moist silver oxide in the dark for 2 hours. The mixture was then filtered, the filtrate cooled with alcohol-carbon dioxide, and the product precipitated by ether (*ca.* 800 c.c.). In this way, bright yellow crystals, appearing pale yellow after filtration and washing with ether, were obtained, having m. p. 66° (decomp.). The material was sparingly soluble in carbon tetrachloride, benzene, dioxan, ether, ethyl acetate, or chloroform, easily soluble in methyl, ethyl, or amyl alcohol, and very soluble in water. Its solutions were pale yellow to yellow depending on the solubility. It coupled readily with aqueous alkaline β -naphthol. The absorption in water is noted (*c*, p. 2084). The solid seemed to be a polyhydrate. It did not give reproducible analyses. Over sulphuric acid it slowly lost weight to a constant value, but the final preparation still contained water and exhibited the solubility behaviour just mentioned.

Anderson and Roedel (*J. Amer. Chem. Soc.*, 1945, **67**, 955) obtained *p*-benzoquinonediaziide by digesting an absolute alcoholic solution of *p*-hydroxybenzenediazonium chloride with silver oxide, filtering, and removing the solvent with dry air at 0°. We obtained it more conveniently (12% yield) by cooling the alcoholic filtrate to -30° (alcohol-solid carbon dioxide). Its properties agreed with those given by Hantzsch and Davidson (*Ber.*, 1896, **29**, 530) and Anderson and Roedel (*loc. cit.*).

Regarding 1:2-naphthaquinone-1-diaziide and its 1:4-isomer, the directions of Anderson and Roedel were followed, except that it proved advantageous to separate the intermediate diazonium hydrogen sulphates instead of the chlorides. In the case of the 1:4-compound it is then unnecessary to convert the salt into the nitrate before extraction. The m. p.s observed were 94–95° and 123°, and yields obtained were 43% and 19%, respectively. 1:2-Naphthaquinone-2-diaziide (yield 50%; *cf.* Orton, *Chem. News*, 1903, **87**, 20) had m. p. 75–76.5°, although Orton as well as Anderson and Roedel quote 77°.

4-Nitro-1:2-naphthaquinone-1-diaziide (Morgan and Evans, *J.*, 1919, **115**, 1126) decomposed with frothing at 130°. Morgan and Evans give 130–134° "with intumescence." Our yield was 51%. 4-Nitro-1:2-benzoquinone-2-diaziide (yield, 45%; Griess, *Annalen*, 1860, **113**, 212) exploded sharply at 127°. Noelting and Steimle (*Bull. Soc. chim.*, 1915, [iv], **17**, 392) mention explosion at 118°, whilst Griess notes violent explosability at 100°.

The above substances were all recrystallised from the solvents prescribed by the authors cited.

Benz-1-thia-2:3-diazole.—2:2'-Dinitrodiphenyl disulphide (Blanksma, *Rec. Trav. chim.*, 1901, **20**, 127; 7 g.) was reduced by tin and hydrochloric acid, etc., as described by Claasz (*Ber.*, 1912, **45**, 1029). After precipitation of the tin by hydrogen sulphide, filtration, and concentration to one-fifth volume, cooling to 5°, and diazotisation (NaNO_2 ; 5 g.), the mixture was steam-distilled. The total condensate was extracted with ether, and the product (yield calc. on disulphide, 50%) recovered by evaporation. Its m. p. was 35° in agreement with that given by Jacobson (*cf.* Beilstein, "Handbuch," XXXVII, 568, for references).

Dipole Moment Estimations.—For these, apparatus and methods already described (*cf.* Calderbank and Le Fèvre, *J.*, 1948, 1949) have been utilised, benzene being the solvent throughout. The symbols used in Tables VI–VIII have been defined in many previous papers (or see "Dipole Moments," 2nd Edn., Methuen, 1948, pp. 39–42).

Because of their relevance the following unpublished data for "azibenzil," $\text{CPh}(\text{N}_2)\cdot\text{COPh}$, are added. They were obtained in collaboration with Mr. C. C. Caldwell at University College, London, 1939, a Pulfrich refractometer being used, with a divided cell, and other components as in "Dipole Moments," 2nd Edn., Methuen, 1948, Ch. II.

$10^6 \times w_1$.	ϵ_{25} .	d_4^{25} .	ρ_{12} .	P_1 .	n_D^{25} .	r_{12} .	$[R_L]_D$.
0	2.2725	0.87378	0.34086	—	1.49360	0.33294	—
5,150	2.2937	0.87498	0.34425	226.1	—	—	—
9,170	2.3106	0.87601	0.34708	226.2	1.49471	0.33270	68.1
14,050	2.3312	0.87720	0.35038	226.0	1.49530	0.33262	68.9
18,020	2.3479	0.87818	0.35301	225.3	1.49577	0.33251	68.6
26,480	2.3839	0.88022	0.35863	224.6	1.49677	0.33231	68.6

Molecular Refractions.—Owing to conjugation a quinonoid form such as (III) should, compared with its cyclic isomeride, *e.g.*, (I), show marked exaltation of molecular refraction. No data are on record

TABLE VI.
 Dielectric-polarisation Measurements.

$10^6 \times w_1$.	ϵ_{25} .	d_4^{25} .	$\alpha\epsilon_2$.	βd_2 .	$10^6 \times w_1$.	ϵ_{25} .	d_4^{25} .	$\alpha\epsilon_2$.	βd_2 .
0	2·2725	0·87378	—	—					
3 : 5-Dibromo-1 : 2-benzoquinone-2-diazide.									
4,325	2·2884	0·87600	3·68	0·513	2,505	2·3026	0·87445	12·02	0·268
7,850	2·3025	0·87790	3·82	0·525	2,849	2·3069	—	12·07	—
10,161	2·3125	0·87912	3·94	0·526	3,670	2·3165	0·87488	11·99	0·300
12,563	2·3221	0·88050	3·95	0·535	4,092	2·3222	0·87503	12·15	0·306
14,556	2·3303	0·88158	3·97	0·522					
1 : 2-Naphthaquinone-1-diazide.									
2,425	2·3005	0·87442	11·56	0·264	2,193	2·3251	0·87450	23·98	0·328
2,949	2·3068	0·87454	11·64	0·258	2,555	2·3325	0·87464	23·48	0·337
4,899	2·3256	0·87519	10·84	0·288	3,438	2·3555	0·87481	24·14	0·300
7,283	2,3470	0·87574	10·23	0·269					
1 : 2-Naphthaquinone-2-diazide.									
3,707	2·3041	0·87481	8·52	0·278	2,846	2·3022	0·87465	10·45	0·306
4,339	2·3098	0·87500	8·60	0·281	5,484	2·3300	0·87541	10·48	0·297
6,654	2·3304	0·87567	8·70	0·284	5,988	2·3350	0·87559	10·44	0·302
					6,716	2·3429	0·87583	10·49	0·305
4-Nitro-1 : 2-naphthaquinone-1-diazide.									
1,586	2·2902	0·87436	11·16	0·366					
1,664	2·2917	0·87435	11·54	0·343					
2,709	2·3033	0·87476	11·37	0·362					
2,723	2·3034	0·87472	11·35	0·345					

 TABLE VII.
 Refraction measurements.

$10^6 \times w_1$.	n_D^{25} .	d_4^{25} .	r_{12} , c.c.	$[R_L]_D$, c.c.
0	1·4964	0·87350	0·33465	—
3 : 5-Dibromo-1 : 2-benzoquinone-2-diazide.				
11,550	1·4988	0·87985	0·33360	67·7
$10^6 \times w_1$.	n_D^{25} .	d_4^{25} .	r_{12} , c.c.	$[R_L]_D$, c.c.
0	1·4980	0·87378	0·33546	—
1 : 2-Naphthaquinone-1-diazide.				
16,030	1·5010	0·87833	0·33543	56·7
1 : 2-Naphthaquinone-2-diazide.				
10,050	1·5000	0·87675	0·33546	57·1
4-Nitro-1 : 2-naphthaquinone-1-diazide.				
10,970	1·4998	0·87764	0·33501	63·3
1 : 4-Naphthaquinonediazide.				
3,409	1·4990	0·87483	0·33563	65·5
Benz-1-thia-2 : 3-diazole.				
18,910	1·5003	0·87957	0·33456	39·2

 TABLE VIII.
 Calculation of results.

	M .	Mean $\alpha\epsilon_2$.	Mean β .	∞P_1 , c.c.	$[R_L]_D$, c.c.	μ , D.
3 : 5-Dibromo-1 : 2-benzoquinone-2-diazide	227·9	3·87	0·600	240·1	67·7	2·8 ₉
1 : 2-Naphthaquinone-1-diazide	170·2	11·07	0·308	394·4	56·7	4·0 ₄
1 : 2-Naphthaquinone-2-diazide	170·2	8·61	0·322	314·9	57·1	3·5 ₃
4-Nitro-1 : 2-naphthaquinone-1-diazide	215·2	11·37	0·405	503·7	63·3	4·6 ₂
1 : 4-Naphthaquinonediazide	170·2	12·06	0·332	424·7	65·5	4·1 ₇
<i>p</i> -Benzoquinonediazide	120·0 ₅	23·87	0·368	564·7	(52) *	4·9 ₈
Benz-1-thia-2 : 3-diazole	136·2	10·46	0·346	298·3	39·2	3·5 ₄
"Azibenzil"	222·1	4·18	0·278	229·3	68·7	2·7 ₉

* Estimated from the refraction of the dibromo-derivative.

for *o*-benzoquinone, but for *p*-benzoquinone the $(R_L)_D$ observed in benzene solution exceeds the calculated value by *ca.* 4 units (Le Fèvre and Le Fèvre, *J.*, 1935, 1696); for phenanthraquinone the corresponding quantity is 5 units.

The measured $[R_L]_D$ for benzthiadiazole is 39—40 c.c. (Table VIII). To check this, the refractivity of the $-N=N-$ system is required. According to Auwers and Heimke (*Ber.*, 1928, **61**, 1030) this is *ca.* 3.2 c.c. for a non-conjugated azo-group. However, later studies in quinoline or α -methylnaphthalene solutions (Auwers, *Ber.*, 1938, **71**, 611) have shown *cis*-azobenzene to have $[R_L]_D = 59.3$; since $C_6H_6 = 26.1$ and $H = 1.1$, the *cis*-azo-configuration must be equivalent to 9.3 c.c. Taking these figures, we calculate for benzthiadiazole $[R_L]_D = 23.9 + 9.3 + 7.8$ (for bivalent sulphur) = 41.0. This is of the order found. On the other hand, a parallel calculation for formula (I), in which $O = 1.6$ (*i.e.*, "ether" oxygen) is used, leads to $[R_L]_D = 34.8$, which minus $2.2 (2 \times H)$ plus $17.8 (2 \times Br) = 50.4$ c.c. Yet the value we record for 3 : 5-dibromo-1 : 2-benzoquinone-2-diazide is 67.7 c.c.—an apparent exaltation of 17.3 c.c. The naphthaquinonediazides of Table VII similarly show exaltations of 10—20 c.c. These are surprisingly large estimates, reminiscent of Smedley's measurements on diphenylbutadiene and diphenylhexatriene (exaltations of 15 and 24, respectively; *J.*, 1908, **93**, 376). The refractivity appropriate to an " $-N_2-$ " group is evidently sensitively dependent upon environment. Thus in azibenzil ($[R_L]_D = 68.7$, present work), $-N_2-$ appears as $68.7 - 50 (2 \times C_6H_5) - 4.84 (2 \times C) - 2.21$ (ketonic oxygen) = 11.7, in ethyl diazoacetate as $28.7 - [22.2_5(\text{for } CH_3 \cdot CO_2Et) - 2.2 (2 \times H)] = 8.7$ (Wolf, *Physikal. Z.*, 1930, **31**, 227; Brühl, *Z. physikal. Chem.*, 1895, **16**, 214) and in di-*p*-chlorophenyldiazomethane as $81 - (62.2 - 2.2) - 2.4 = 18.6$ c.c. ($C_6H_5Cl = 31.1$, and the diazo-compound = 81 for light of λ 5790; Sidgwick, Sutton, and Thomas, *loc. cit.*; unreferenced *R* data are from Landolt-Börnstein's "Tables").

We acknowledge gratefully financial assistance from the Commonwealth Science Fund and the continued use of apparatus originally provided by the Research Committee of the Chemical Society.

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[Received, February 21st, 1949.]