610. *The Possibility of Geometrical Isomerism among the 1-Aryl-3 : 3-dimethyltriazens.*

By Raymond J. W. Le Fèvre and Thomas H. Liddicoet.

The dipole moments and ultra-violet absorption spectra of about a dozen 1-aryl-3 : 3-dimethyltriazens have been determined. The known forms of these substances appear to possess *trans*-configurations about the $-N{=}N-$ group. The mesomeric polarisations run parallel to those noted in the literature for dimethylaniline and its derivatives. Exposure to sunlight causes mainly photodecomposition but, beneath the dielectric constant and spectrometric evidence of this, slight indications are observable which resemble phenomena shown by other azo-derivatives and which would not be inconsistent with the occurrence of a reversible *trans* $\rightleftharpoons$ *cis* change.

ACCORDING to Hantzsch's views regarding the stereostructure of the azo-group, *cis–trans*-isomers should exist among the diazo-carboxyamides (R·N:N·CO·NH₂), the triazens (R·N:N·NHR and R·N:N·NR₂), the diazosulphones (R·N:N·SO₂·R), the diazo-ethers (R·N:N·OR), the diazo-sulphides (R·N:N·SR), etc. Despite past efforts to demonstrate such isomerism, the general conclusion seems to have been that known representatives of these classes occur only as single forms (see below; also Saunders, " The Aromatic Diazo-compounds and Their Technical Applications," 2nd Edn., E. Arnold & Co., London, 1949, pp. 139, 192, 387, 391). However, recently (*J.*, 1951, 1977) new evidence has been produced which indicates that certain diazo-carboxyamides do in fact undergo geometrical inversion under the action of light, and that the process is reversed in the dark.

We now report an examination of the aryldimethyltriazens recorded in Tables I and II.

TABLE I.

Polarisations at infinite dilution in benzene at 25°, and apparent dipole moments of 1-aryl-3 : 3-dimethyltriazens.

Ar in Ar·N:N·NMe₂	M_1	$\alpha\varepsilon_2$	β	$_T P_\infty$ (c.c.)	R (c.c.)	μ, D
C₆H₅	149·1	4·14	0·135	160	53	2·2₈
o-Cl·C₆H₄	183·6	5·14	0·254	224	58	2·8₅
m-Cl·C₆H₄	183·6	7·54	0·190	311	58	3·5₂
p-Cl·C₆H₄	183·6	9·86	0·259	387	58	4·0₁
p-Br·C₆H₄	228·0	7·57	0·379	373	60	3·9₁
o-NO₂·C₆H₄	194·1	10·9₅	0·355	442	62	4·3₁
m-NO₂·C₆H₄	194·1	18·8	0·223	738	59	5·76
p-NO₂·C₆H₄	194·1	28·1	0·262	1075	59	7·0₄
p-Me·C₆H₄	163·1	2·75	0·092	135	57	1·9₅
p-MeO·C₆H₄	179·1	3·53	0·205	167	59	2·3₀
o-C₆H₅·C₆H₄	225·1	2·99	0·191	189	79	2·3₂
p-C₆H₅·C₆H₄	225·1	3·75	0·215	219	79	2·6₁
β-C₁₀H₇	199·1	3·63	0·249	187	71	2·3₈

Dissolved in benzene, these substances seem to suffer a slow photo-decomposition when exposed to sunlight—a conclusion supported both by dielectric constant and spectrometric determinations (see Experimental). From Table IV it will be noted that the dielectric constant is not always raised by irradiation, *e.g.*, with the *o*- and the *p*-nitrophenyl derivative decreases of *ca.* 0·01 unit occur. Subsequent storage in the dark tends to cause either no significant change or a further increase of ε; the *m*-nitrophenyltriazen is an exception in that darkness slightly over-compensates the initial alteration of dielectric constant. With the *o*- and *m*-nitrophenyl compounds there are also indications that re-irradiation of the " restored " (3rd Col., Table IV) solutions has, in smaller measure, qualitatively the same effect as with a fresh solution.

The data of Table IV would be understandable if irreversible destruction of solute were in varying degrees accompanied by reversible formation of a *cis*-isomer, *i.e.*, (I) $\rightleftharpoons$ (II). Unfortunately neither the relative polarities of (I) and (II) nor the directions of action of their

(I.)

(II.)

(III.)
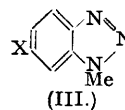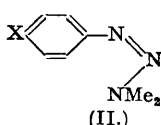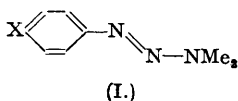
molecular resultants can be forecast with certainty. When X = H the moment of (II) should approach the magnitude of that of benzotriazole ($\mu = 4\cdot07$ D.; Jensen and Friediger, *Kgl. Danske Vidensk. Selsk.*, 1943, **20**, No. 20) or, more relevantly, that of the *N*-methyl derivative (III) ($\mu = 4\cdot16$ D., present work). A rise in moment, and hence in ε_{12}, during the transformation of (I) into (II) therefore seems likely. With other groups in various positions predictions of μ_{I} and μ_{II} are impossible on present knowledge.

In the preceding remarks we have assumed that as prepared these triazens have the *trans*-configuration (I). Table I lists the apparent dipole moments calculable from measurements taken before exposure to sunlight.

It is clear that, for a range of groups X, only forms extended as (I) should be smoothly related by polarity to the corresponding substituted dimethylanilines. Since no values for *o*- and *m*-derivatives of dimethylaniline have been reported to date (Marsden and Sutton, *J.*, 1936, 599) we quote also values for the appropriate anilines (cf. Wesson, M.I.T. Tables, 1948) :

Substituent	H	*p*-Me	*o*-Cl	*m*-Cl	*p*-Cl	*p*-Br	*o*-NO$_2$	*m*-NO$_2$	*p*-NO$_2$
C$_6$H$_5$·N:N·NMe$_2$	2·3	1·9$_5$	2·8$_5$	3·5	4·0	3·9	4·3	5·8	7·0
C$_6$H$_5$·NMe$_2$	1·6	1·3	1·3	—	3·3	3·4	—	—	6·9
C$_6$H$_5$·NH$_2$	1·5	1·3	1·8	2·7	3·3	3·9	4·3	5·0	6·3

A satisfactory parallelism is noted, the moments of the triazens surpassing those of the amines in all cases except when an *o*-nitro-group is present. It is evident that the $-$N$_2$·NMe$_2$ fragment carries a component moment whose negative pole is towards the aryl nucleus and that mesomeric polarisations of the type shown in (IV) are also operative. The differences between the moments of derivative and of parent are roughly the same in the triazen as in the aniline series. The exceptional *o*-nitro-products have structures such that mesomerism will be sterically inhibited (compare Remington, *J. Amer. Chem. Soc.*, 1945, **67**, 1838). As information on the last point might be available from the ultra-violet spectra the prominent features of these are listed (Table II).
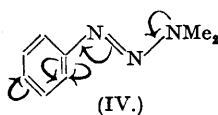
TABLE II.

Absorption maxima and inflexions.

Ar in Ar·N:N·NMe$_2$	$\lambda_{max.}$ (log$_{10}$ $\varepsilon_{max.}$)		
C$_6$H$_5$	225 (3·97)	285 (4·14)	308 (4·11) *
p-Me·C$_6$H$_4$	225 (3·98)	285 (4·15)	313 (4·13)
p-Br·C$_6$H$_4$	<230 (>3·93)	291 (4·29)	320 (4·27)
p-MeO·C$_6$H$_4$	ca. 222 (3·95)	288 (4·12)	324 (4·07)
o-CO$_2$H·C$_6$H$_4$	240 (4·06)	—	{ 320 (4·19) { 338 (4·13) *
o-Cl·C$_6$H$_4$	232 (4·02)	{ 281 (4·10) * { 289 (4·12)	311 (4·04) *
m-Cl·C$_6$H$_4$	232 (4·07)	{ 285 (4·11) * { 292 (4·13)	309 (4·09) *
p-Cl·C$_6$H$_4$	<224 (>3·94)	287 (4·18)	314 (4·15)
o-NO$_2$·C$_6$H$_4$	<224 (>4·03)	ca. 280 (4·10) *	295 (4·13)
m-NO$_2$·C$_6$H$_4$	<225 (>3·92)	{ 277 (4·22) * { 286 (4·25) { 290 (4·23) *	300 (4·18) *
p-NO$_2$·C$_6$H$_4$	240 (3·90)	275 (3·55)	360 (4·33)
o-C$_6$H$_5$·C$_6$H$_4$	<232 (>4·10) 255 (4·25)	292 (4·12)	299 (4·12) *
p-C$_6$H$_5$·C$_6$H$_4$	<240 (>3·81)	—	{ ca. 305 (4·27) * { ca. 325 (4·31)
β-C$_{10}$H$_7$	<226 (>4·20)	{ 252 (4·19) { ca. 272 (4·31) { 280 (4·29) *	315 (4·23)

* Inflexion.

In general, aromatic azo-compounds absorb in three regions : below 250, from 300 to 350, and above 400 mμ. (cf. Cook, Jones, and Polya, *J.*, 1939, 1315; Winkel and Siebert, *Ber.*, 1941, **74**, 675; Le Fèvre and Wilson, *J.*, 1949, 1106; Freeman and Le Fèvre, *J.*, 1951, 415; Le Fèvre and Worth, *ibid.*, 1814). When pure, the triazens are all pale yellow, corresponding to bands in the blue end of the visible spectrum. The situation revealed by Table II is therefore unexceptional. Precedents are known for the occurrence of *two* maxima near 300 mμ., *e.g.*, the nitrobenzenediazocyanides (*J.*, 1949, 1106) are analogous to the nitro-triazens in this
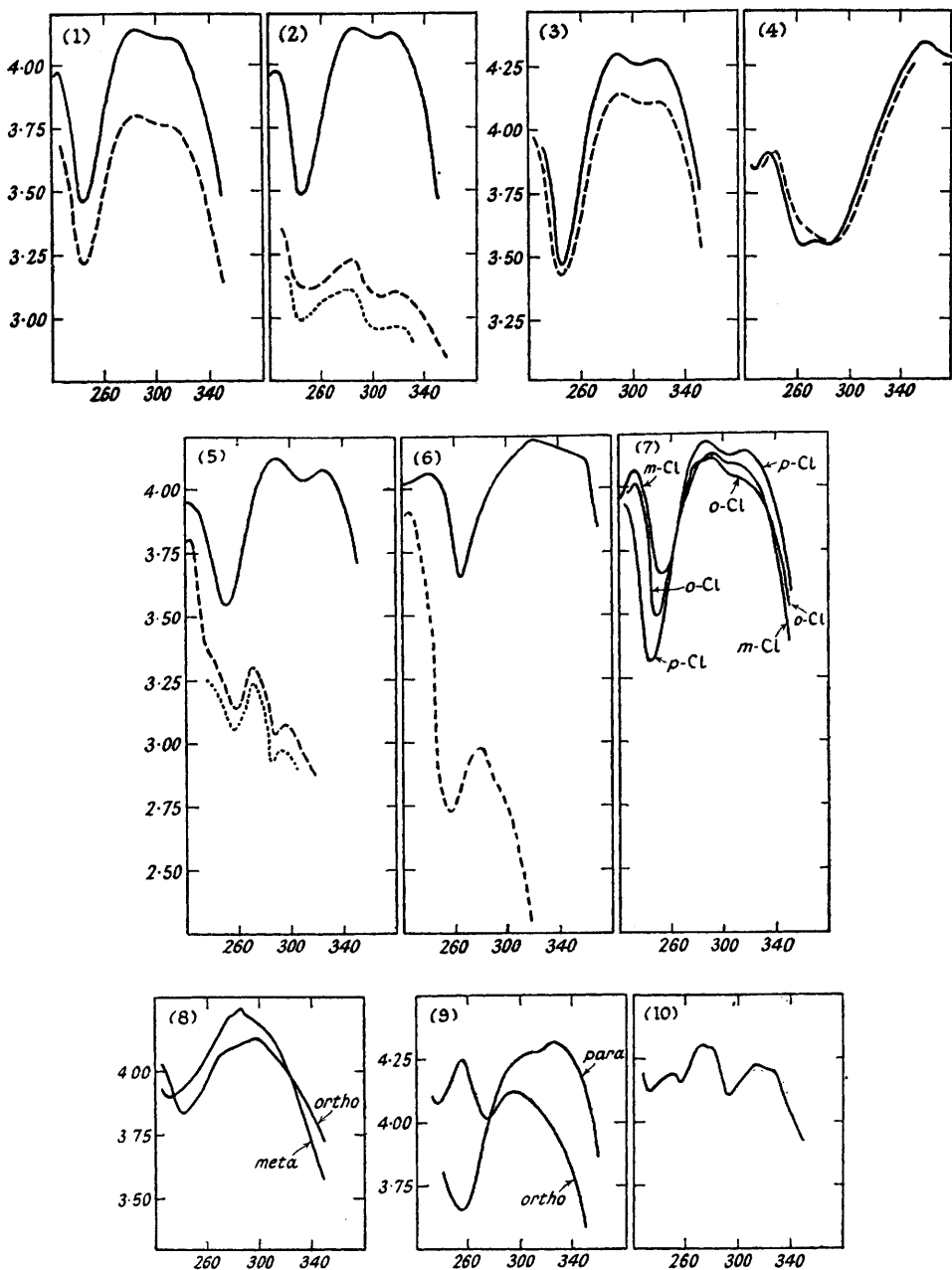
Curve.	1-Substituent.	Concn., (mol./l.) × 10⁶.	Curve.	1-Substituent.	Concn., (mol./l.) × 10⁶.
1	Ph	102	7	m-Cl·C$_6$H$_4$	98·4
2	p-Me·C$_6$H$_4$	76·2	7	p-Cl·C$_6$H$_4$	100
3	p-Br·C$_6$H$_4$	87·3	8	o-NO$_2$·C$_6$H$_4$	59·6
4	p-NO$_2$·C$_6$H$_4$	99	8	m-NO$_2$·C$_6$H$_4$	81·4
5	p-MeO·C$_6$H$_4$	100	9	o-Ph·C$_6$H$_4$	97
6	o-CO$_2$H·C$_6$H$_4$	88·4	9	p-Ph·C$_6$H$_4$	112
7	o-Cl·C$_6$H$_4$	105	10	β-C$_{10}$H$_7$	92·4

————— Original. — — — — After 4 hours' exposure.
------- Exposed solution after 24 hrs. in darkness.

respect. The " K-bands " (with $\log_{10} \varepsilon$ usually *ca.* 4), ascribed to general conjugation between the $-N{=}N-$ system and the aryl nuclei, commonly lie at wave-lengths *longer* than 300 mμ. Such a view applied to the present data makes interpretation possible : the " K-band " in the parent $C_6H_5 \cdot N{:}N \cdot NMe_2$ is at 300 mμ.; as resonance increases through various *p*-substituents the $\lambda_{max.}$ rises, up to 360 mμ. for the *p*-nitro-derivative; where there is " steric inhibition of resonance," as with the *o*-chloro-, *o*-nitro-, and *o*-phenyl derivatives, the $\lambda_{max.}$ drops back, and in the last two instances falls below 300 mμ. The results for $o\text{-}CO_2H \cdot C_6H_4 \cdot N{:}N \cdot NMe_2$ appear abnormal on this simple steric basis; they can however be understood if, owing to the presence of a carboxyl group, the molecule tends to exist as an internal salt, Burawoy (*J.*, 1937, 1865) having shown that the addition of a hydrogen nucleus to an azo-K-chromophore has a strong effect in displacing the corresponding K-bands to longer wave-lengths. Incidentally, Burawoy also records a spectrum of benzeneazopiperidine in hexane with a maximum at 289·5 mμ. ($\log_{10} \varepsilon = 4·20$); the form of the curve is not quite symmetrical and could well be covering a minor peak or inflexion at *ca.* 310 mμ., in harmony with the triazens of Table II.

Finally, regarding the use of (III; X = H) as a rough model for the unknown *cis*-triazens (II), it is relevant that Macbeth and Price (*J.*, 1936, 111) found 1-methylbenzo-1 : 2 : 3-triazole to absorb at 258·5 (3·79), 279·5 (3·59), and 291·5 mμ. (3·45)—the last being an inflexion. The two longer-wave bands were associated by these authors with the Ar$\cdot$N$:$N$\cdot$N arrangement, *i.e.*, were " K-bands." They occurred at shorter wave-lengths (and with lower intensities) than those now observed for $C_6H_5 \cdot N{:}N \cdot NMe_2$ (Table II). Among azo-derivatives the change *trans* $\longrightarrow$ *cis* commonly alters the absorption at *ca.* 300 mμ. in the same sense (cf. Le Fèvre and Wilson, *J.*, 1949, 1106). The fact that the double maximum (285, 308 mμ.) observed for $C_6H_5 \cdot N{:}N \cdot NMe_2$ (curve 1) is not detectably shifted along the λ scale by irradiation therefore suggests—as do the ε changes (Table IV)—that the *cis*-content so produced is small.

From the above evidence we draw the conclusions set out in the summary. It may be recalled that a *trans*-configuration of the $-N{=}N-$ unit was likewise inferred for the diazoamino-benzenes examined by Le Fèvre and Vine (*J.*, 1937, 1805).

In the Experimental part we describe tests which show that, even in dry benzene, these triazens slowly interact with β-naphthol to yield azo-dyes, the process being slightly accelerated by sunlight. Previously Hauser and Breslow (*J. Amer. Chem. Soc.*, 1941, **63**, 418) had demonstrated an analogous reaction between benzeneazopiperidine and β-naphthol in dry pyridine, a medium the use of which suggested that the coupling was unusually difficult (cf. Saunders, *op. cit.*, p. 224).

<div align="center">EXPERIMENTAL.</div>

Solutes.—All the triazens used have been prepared by the method given by Elks and Hey (*J.*, 1943, 441). The m. p.s or b. p.s of the samples used agreed with those recorded in the literature (cf. Beilstein, " Handbuch " der Organischen Chemie," Vol. 16, pp. 686, 705; Elks and Hey, *loc. cit.*; Johnson, *J.*, 1946, 898; Hunter, *J.*, 1937, 324) except in the cases of those recorded in the Table, which do not appear

Aryl	B. p./mm. or m. p.	N, %, Found	Formula	N, %, Calc.
p-C$_6$H$_4$Cl	164—166°/27—28	23·2	C$_8$H$_{10}$N$_3$Cl	22·9
m-C$_6$H$_4$Cl	148—151°/20	22·6	,,	22·9
o-NO$_2$·C$_6$H$_4$	31—32° *	29·0	C$_8$H$_{10}$O$_2$N$_4$	28·9
p-OMe·C$_6$H$_4$	174—177°/29	23·4	C$_9$H$_{13}$ON$_3$	23·5
o-Ph·C$_6$H$_4$	143—145°/1	18·4	C$_{14}$H$_{15}$N$_3$	18·7
p-Ph·C$_6$H$_{14}$	70—71° †	18·85	,,	18·7

<div align="center">* Pale yellows prisms from light petroleum (b. p. 60—90°).
† Buff-coloured plates from aqueous alcohol.</div>

to have been described previously and, unless otherwise specified, are pale yellow oils. 1-Methylbenzo-1 : 2 : 3-triazole was obtained from benzotriazole (*Org. Synth.*, 1940, **20**, 16), by use of methyl sulphate (Krollpfeiffer, Rosenberg, and Mülhausen, *Annalen*, 1934, **515**, 124). Recrystallised from ligroin it had m. p. 64°.

Dipole-moment Measurements.—These were made at 25°, with sodium-dried " crystallisable " benzene as solvent, with the apparatus and procedures noted before (*J.*, 1948, 1949; 1949, 333; *re* symbols cf. *Trans. Faraday Soc.*, 1950, **46**, 1, and *J.*, 1937, 1805). Details are set out, under the usual headings, in Table III. Refractivities have been directly determined in only three cases. Values shown in parentheses are derived from the figure obtained for the *p*-tolyl derivative, namely, 57·4 c.c., by noting that—since $R_{Toluene} = 31·1$ and $R_H = 1·1$—the group Me$_2$N·N$:$N— evidently contributes 27·4 c.c., so that the addition of 26·3 to the molecular refractions of benzene (26·2 c.c.), nitrobenzene (32·7 c.c.), chlorobenzene (31·4 c.c.), bromobenzene (34·0 c.c.), anisole (33·0 c.c.), diphenyl (52·4 c.c.), and naphthalene (44·5 c.c.) should give satisfactory estimates. As a check the $R_{calc.}$ for $C_6H_5 \cdot N{:}N \cdot NMe_2$, *viz.*, 52·5 c.c. may be compared with that (52·7 c.c.) obtained from $R_{azobenzene} = 63·7$ c.c. (Auwers, *Ber.*, 1938, **71**, 611), $R_H = 1·1$ c.c., $R_{C_6H_4} = 26·2$ c.c., and $R_{Me_2NH} = 15·2$ (Le Fèvre and Russell, *Trans. Faraday Soc.*, 1947, **43**, 374). For the purposes of Table I, R has been taken to the nearest whole number in each case.

TABLE III.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
0	2·2725	0·87378	—	—	1·4972₅	—

3 : 3-Dimethyl-1-phenyltriazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
7,465	—	0·87476	—	0·150	—
7,816	2·3049	—	4·14	—	—
12,370	2·3243	0·87525	4·19	0·136	—
15,020	2·3344	0·87535	4·12	0·120	—
19,340	2·3521	0·87603	4·12	0·133	—	(52·5)

1-m-Chlorophenyl-3 : 3-dimethyltriazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
6,196	2·3180	0·87459	7·34	0·150	—
14,067	2·3830	0·87572	7·85	0·158	—
20,026	2·4250	0·87737	7·61	0·205	—
26,789	2·4694	0·87954	7·35	0·246	—	(57·7)

1-p-Bromophenyl-3 : 3-dimethyltriazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
6,006	2·3191	0·87569	7·76	0·364	—
9,194	2·3422	0·87718	7·58	0·423	—
12,515	—	0·87761	—	0·350	—
14,146	2·3762	0·87851	7·33	0·383	—
18,597	2·4131	0·87989	7·56	0·376	—
21,451	2·4362	0·88091	7·63	0·380	—	(60·3)

3 : 3-Dimethyl-1-m-nitrophenyltriazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
5,452	2·3754	0·87478	18·9	0·210	1·4975	56·3
7,316	2·4083	0·87515	18·6	0·214	1·4979	60·8
8,022	2·4237	0·87534	18·9	0·223	—	—
11,591	2·4908	0·87628	18·8	0·247	1·4985	61·0

Mean $[R_L]_D$ = 59·4 c.c., calc. = 59·0 c.c.

3 : 3-Dimethyl-1-p-tolyltriazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
3,842	2·2836	0·87408	2·89	0·089	—	—
6,698	2·2916	0·87412	2·85	0·058	1·4978	59·4
9,795	2·2976	0·87465	2·56	0·102	—	—
10,360	2·3003	0·87467	2·69	0·098	1·4983	58·2
20,140	2·3276	0·87574	2·74	0·111	1·4989	55·4

Mean $[R_L]_D$ = 57·4 c.c.

1-o-Diphenylyl-3 : 3-dimethyltriazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
2,878	2·2810	0·87426	2·94₅	0·191	—
3,010	2·2811	0·87427	2·86	0·186	—
5,254	2·2883	0·87466	3·02	0·192	—
6,491	2·2928	0·87488	3·13	0·193	—	(78·7)

1-o-Chlorophenyl-3 : 3-dimethyltriazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
5,692	2·2917	0·87502	5·13	0·249	—
11,733	2·3347	0·87673	5·30	0·288	—
15,189	2·3486	0·87709	5·01	0·244	—
20,471	2·3772	0·87802	5·12	0·237	—	(57·7)

1-p-Chlorophenyl-3 : 3-dimethyltriazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
4,363	2·3158	0·87492	9·92	0·299	—
8,297	2·3543	0·87552	9·86	0·240	—	—
11,160	2·3824	0·87627	9·85	0·255	—
17,000	2·4391	0·87741	9·80	0·244	—	(57·7)

3 : 3-Dimethyl-1-o-nitrophenyltriazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
3,664	2·3113	0·87488	10·6	0·344	1·4974	60·6
4,309	2·3196	0·87506	10·9	0·330	—	—
6,400	2·3452	0·87577	11·4	0·356	1·4984	61·5
7,685	2·3561	0·87633	10·9	0·380	1·4989	64·0

Mean $[R_L]_D$ = 62·0 c.c., calc. = 59·0 c.c.

3:3-Dimethyl-1-p-nitrophenyltriazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
2,570	2·3408	0·87440	26·6	0·276	—
3,015	2·3584	0·87452	28·5	0·281	—
4,036	2·3887	0·87488	28·8	0·312	—
4,856	2·4091	0·87489	28·1	0·273	—
6,404	2·4535	0·87472	28·3	0·168	—	(59·0)

1-p-Methoxyphenyl-3 : 3-dimethyltriazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
4,979	2·2900	0·87467	3·52	0·205	—
7,979	2·3014	0·87531	3·62	0·219	—
8,851	2·3038	0·87537	3·54	0·206	—
17,728	2·3333	0·87672	3·43	0·190	—	(59·3)

1-p-Diphenylyl-3 : 3-dimethyltriazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
14,35	2·2779	0·87405	3·76	0·215	—
5,209	2·2926	0·87478	3·86	0·220	—
6,874	2·2976	0·87507	3·65	0·215	—
8,784	2·3052	0·87538	3·72	0·209	—	(78·7)

3 : 3-Dimethyl-β-naphthyl-1-triazen.

$10^6 w_1$	ε_{12}	d_{12}	αE_2	β	n_{12}	$[R_L]_D$
3,868	2·2866	0·87467	3·65	0·263	—
6,134	2·2950	0·87515	3·67	0·256	—
7,453	2·2995	0·87531	3·62	0·235	—
10,977	2·3118	0·87609	3·58	0·241)	—	(70·8)

TABLE IV.

Changes of ε *through successive illumination and darkness.**

1-Substituent	Initial ε^{25}	After 4 hrs'. daylight	After 20—24 hrs'. darkness	After 4 hrs'. daylight	After 20—24 hrs'. darkness
Ph	2·3521	2·355	2·362	—	—
o-Cl·C₆H₄	2·3486	2·352	2·356	—	—
p-Br·C₆H₄	2·3422	2·347	2·355	—	—
o-NO₂·C₆H₄	2·3561	2·345	2·354	2·351	—
m-NO₂·C₆H₄	2·4908	2·501	2·487	2·490	2·494
p-NO₂·C₆H₄	2·4091	2·394	2·414	—	—
p-Me·C₆H₄	2·3276	2·328	2·328	—	—
p-MeO·C₆H₄	2·3014	2·319	2·318	—	—
p-Ph·C₆H₄	2·3052	2·306	2·305	—	—

* Concns. may be identified *via* ε values in Table III.

Effect of Sunlight on the Dielectric Constants of the Above Solutions.—The ε^{25} values of Table III were obtained on solutions freshly made up in brown bottles. After the initial capacity determinations, the solutions were transferred to clear-glass flasks, exposed to sunlight for 4 hours, and then remeasured. Subsequently, after 20—24 hours' storage in the dark, they were examined again. In the case of the *m*-nitrophenyl derivative, the " light–dark " cycle was performed twice. Sample observations are recorded in Table IV.

Interactions of the Triazens with β-Naphthol.—To β-naphthol (0·5 g.) in benzene (10 c.c. of the solvent used for dipole moment determinations), approx. 0·002 mole of the triazen was added. The mixtures were divided into two portions, one kept in the dark and the other exposed to bright sunlight. Inspections at hourly intervals indicated that illumination accelerated the production of colour. This was particularly noticeable with the *p*-chloro-, *p*-bromo-, *p*-methyl-, and *p*-methoxy-derivatives, and less so with the others.

In view of the possibility (Le Fèvre and Northcott, *Chem. and Ind.*, 1948, 543) that β-naphthol might considerably screen off from the dissolved triazen the wave-band around 300 mμ., three experiments were made, as checks, in which the triazen–benzene mixture was irradiated alone and the naphthol solution added only at the moment of test. However, this alternative procedure did not cause significantly different results.

By partial evaporation of five of these triazen–β-naphthol mixtures crystalline products were isolated. In colours and m. p.s these agreed with descriptions given in Beilstein (" Handbuch der Organischen Chemie," Vol. 16, pp. 162—170) for the expected azo-compounds, $HO·C_{10}H_6·N:N·C_6H_4·X$.

Group X	M. p. (observed)	M. p. (Beilstein)
H	132°	128·5°, 129·5°
		133, 134
p-Cl	155—157	158, 160
p-Br	171	172—173
p-CH₃	133—134	134—135
p-(OCH₃)	139—140	141

The recovered materials did not depress the m. p.s of appropriate authentic specimens.

Absorption Spectra.—These were determined with the Beckman photoelectric spectrophotometer, Model DU, in 95% ethanol as a solvent. Their forms are shown in the figures. Prominent features are listed in Table II.

*The Dipole Moment of 1-Methylbenzo-*1 : 2 : 3-*triazole.*—The necessary measurements (in benzene at 25°) are listed below, as under the first five headings used in Table III :

0	2·2725	0·87378	—	—
1253	2·2911	0·87409	14·8	0·283
2814	2·3131	0·87451	14·4	0·297
3554	2·3222	0·87484	14·0	0·298
5797	2·3553	0·87528	14·3	0·294

Since mean $\alpha\varepsilon_2 = 14·4$ and mean $\beta = 0·293$, $_{\infty}P_1 = 393$ c.c. The molecular refraction (D line) has already been determined in quinoline solution by von Auwers (*Ber.*, 1938, **71**, 604) as 38·23 c.c. Accordingly the apparent moment of 1-methyl-1 : 2 : 3-benztriazole is $4·1_6$ D.