[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF CALIFORNIA, LOS ANGELES]

The Absorption Spectra of Some Aromatic Triazenes

BY BRUCE F. DAY,[1a] TOD W. CAMPBELL[1b] AND G. M. COPPINGER[1b]

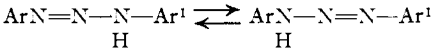
The spectra of nineteen variously substituted derivatives of 1,3-diphenyltriazene have been determined in an attempt to elucidate the problem of the structure of aromatic triazenes in solution by a study of their absorption spectra. However, no conclusive argument regarding structure can be drawn from an examination of their spectra.

The problem of the structure of aromatic triazenes has intrigued chemists since it was first observed that the coupling of two dissimilar aromatic amines *via* diazotization of one, followed by addition of the other gave the same crystalline compound, no matter which of the amines was diazotized.

$$ArN_2^+ + Ar^1NH_2 \longrightarrow ArN_3HAr^1 \longleftarrow ArNH_2 + Ar^1N_2^+$$

No completely satisfactory answer to the problem of the structure of these compounds either in solution or in the solid state has been presented, even though there is an extensive literature on the subject.[2]

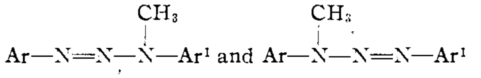
From an examination of the pertinent literature, it would appear that ultraviolet absorption spectra might afford a method for determination of the nature of the triazene in solution. If the triazene exists as a mixture of tautomers it should be possible to determine the nature of the mixture and



$$ArN{=}N{-}\underset{H}{N}{-}Ar^1 \rightleftharpoons Ar\underset{H}{N}{-}N{=}N{-}Ar^1$$

the position of equilibrium provided (1) the spectra of the individual tautomers can be obtained and (2) the spectra of the tautomers are significantly different. Many instances may be cited in which such a situation obtains in a similar carbon system. Thus mixtures of allylbenzene and propenylbenzene and their derivatives can be analyzed by their spectra,[3,4] while photoisomerization of dienes[5] and carotene[6] have been followed similarly. Other examples too numerous to mention can be found in the literature.

It was assumed as a first approximation that the spectra of the individual triazene tautomers would be similar to those of the corresponding N-methyl derivatives where no tautomerism is possible.



$$Ar{-}N{=}N{-}\overset{CH_3}{N}{-}Ar^1 \text{ and } Ar{-}\overset{CH_3}{N}{-}N{=}N{-}Ar^1$$

A series of appropriately substituted triazines was prepared and the absorption spectra of these compounds were measured in cyclohexane. The data are recorded in Fig. 1 and in Table I.

The spectra of all of the compounds examined (excepting the nitro derivative) were very similar, both as to the position and the intensity of the maxima. In general, the compounds showed

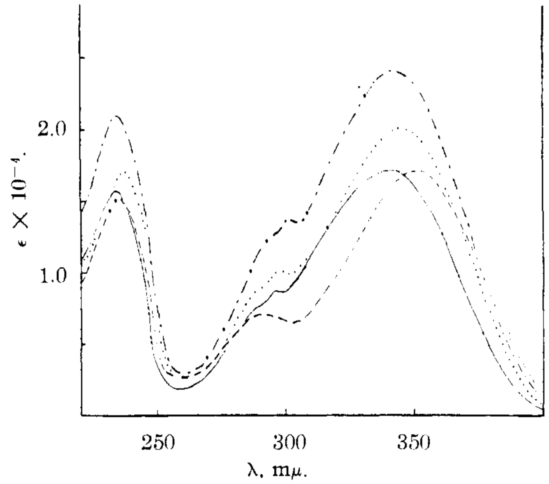
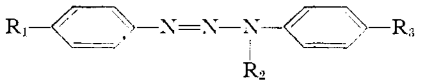


Fig. 1.—Absorption spectra of some aromatic triazenes: ——, $C_6H_5N{=}N{-}\underset{CH_3}{N}{-}C_6H_5$; — — —, $p\text{-}CH_3C_6H_4NH{-}N{=}N{-}C_6H_4CH_3\text{-}p$; — · — $C_6H_5N{=}N{-}\overset{CH_3}{N}{-}C_6H_5CH_3\text{-}p$; ……, $p\text{-}CH_3C_6H_4N{=}N{-}\overset{CH_3}{N}{-}C_6H_5CH_3\text{-}p$.

TABLE I

ABSORPTION MAXIMA FOR VARIOUS TRIAZENES



Compound R1	R2	R3	1st maximum mμ	1st maximum ε × 10⁻⁴	2nd maximum mμ	2nd maximum ε × 10⁻⁴	3rd maximum mμ	3rd maximum ε × 10⁻⁴
H	H	H	346	1.82	287 293	0.77 0.77	238	1.80
CH_3O-	H	H	357	2.22	290–296	1.05	236	1.70
Cl	H	H	351	2.17	290	1.05	236	1.96
CH_3	H	H	350	1.75	290–295	0.71	237	1.50
CF_3	H	H	347	1.99	294	0.78	234	1.54
NO_2	H	H	321	2.46	.....	..	226	1.49
CH_3O	H	CH_3O	362	1.84	301	1.17	239	1.20
Cl	H	Cl	356	2.23	298	1.02	238	1.74
CH_3	H	CH_3	355	2.19	295	0.99	238	1.69
CF_3	H	CF_3	345	2.25	294	0.81	234	1.92
H	CH_3	H	340	1.78	294	1.34	235	1.90
CH_3O	CH_3	H	350	1.86	298	1.03	237	1.29
Cl	CH_6	H	346	2.29	295	1.03	238	1.99
CH_3	CH_3	H	345	2.08	295	1.24	237	1.75
CF_3	CH_3	H	344	1.98	.....	..	236	1.76
H	CH_3	CH_3O-	345	1.97	311	1.46	238	1.86
H	CH_3	CH_3	342	2.48	302	1.43	235	2.23
Cl	CH_3	Cl	350	2.24	304	1.18	240	1.74
CH_3	CH_3	CH_3	348	2.08	302	1.23	238	1.77

three maxima, at approximately 350, 290 and 238 mμ. The latter two bands are presumably the bands characteristic of aromatic amines, somewhat intensified and altered by substitution of the N-arylazo group. This similarity can be seen more clearly by an examination of the data in Table II. The band at about 350 mμ is presumably due to the

---

[1] (a) E. I. du Pont de Nemours Experimental Station, Wilmington, Delaware; (b) Western Regional Research Laboratory, Albany 6, California.

[2] T. W. Campbell and B. F. Day, *Chem. Revs.*, **48**, 299 (1951).

[3] T. W. Campbell, S. Linden, S. Godshalk and W. G. Young, THIS JOURNAL, **69**, 880 (1947).

[4] T. W. Campbell and W. G. Young, *ibid.*, **71**, 296 (1949).

[5] Y. Hirshberg, E. Bergmann and F. Bergmann, *ibid.*, **72**, 5720 (1950).

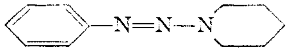
[6] F. Stitt, E. M. Bickoff, G. F. Bailey, C. R. Thompson and S. Friedlander, *J. Assoc. Official Agr. Chem.*, in press.

TABLE II

ABSORPTION SPECTRUM OF R——NH$_2$

R	Maxima λ (mμ)	ε	λ (mμ)	ε
H	235	7100	283	1500
CH_3	237	8000	293	1840
Cl	241	8500	298	1590
CF_3	244	10700	285	1360
OCH_3	237	9300	305	2900

ArN=N group. The position of this high-intensity band is shifted considerably from its observed position in such compounds as benzeneazomethane (λ 2595 Å., ε 7800) and azobenzene (λ 3130 Å., ε 20000).[7] This is presumably due at least in part to the extended separation of charge in the possible excited states of the triazene. This cannot account completely for the shift, however, since N-benzeneazopiperidine, capable of similar resonance, has its maximum[7] at λ 2895 Å.; ε 16000,



higher than benzeneazomethane, but lower than either azobenzene or the triazenes listed in Table II.

Such has been suggested by Hunter as contributing to the structure of the triazenes.[8,3]

Experimental Part

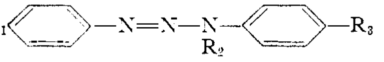
Preparation of Triazenes.—Symmetrical triazenes were prepared according to the procedure of Hartman and Dickey.[9]

To prepare unsymmetrical triazenes, derived from two different aromatic amines, the first amine was diazotized and the solution buffered with sodium acetate. The second amine was then added to this buffered solution, and the mixture was stirred rapidly for a period of time sufficient to allow complete reaction. The precipitated triazene then was filtered and purified.

Purification of Triazenes.—A chromatographic column 30 cm. by 4 cm. was filled with 100–140 mesh alumina (Harshaw), which had been activated by heating for several hours at 250°, and washed with 500 ml. of dry hexane. About 2 g. of crude dry triazene in 50 ml. of hexane (containing enough benzene to ensure complete solution) was placed on the column and developed with hexane. A bright yellow band of triazene moved slowly down the column, while several red and brown bands remained near the top. The yellow triazene fraction was removed by elution and recrystallized once from a suitable solvent, usually hexane. These compounds can be stored for long periods of time in the cold and in the absence of light when purified in this manner.

Physical data on the compounds prepared are given in Table III.

TABLE III

PHYSICAL AND PREPARATIVE DATA ON TRIAZENES 

R_1	R_2	R_3	M.p., °C. (cor.)	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Empirical formula
H	H	H	99.3–100.3	73.07	72.83	5.62	5.88	$C_{12}H_{11}N_3$
H	H	$-CF_3$	117.2–117.6	58.87	58.93	3.80	3.97	$C_{13}H_{10}N_3F_3$
CF_3	H	$-CF_3$	119.1–119.3	50.46	50.59	2.72	2.88	$C_{14}H_9N_3F_6$
H	CH_3	CH_3	28	74.64	74.77	6.71	6.92	$C_{14}H_{15}N_3$
CH_3	CH_3	H	67–67.8	74.64	74.70	6.71	6.90	$C_{14}H_{15}N_3$
Cl	CH_3	H	86.7–88.1	63.54	63.49	4.92	4.92	$C_{13}H_{12}N_3Cl$
CF_3	CH_3	H	86.0–86.9	60.21	59.97	4.33	4.39	$C_{14}H_{12}N_3F_3$
H	CH_3	H	Oil	73.91	73.88	6.20	6.31	$C_{13}H_{13}N_3$
CH_3	CH_3	CH_3	101.7–102.5	75.28	75.40	7.16	7.26	$C_{15}H_{17}N_3$
CH_3O-	CH_3	CH_3O-	103–103.9	66.40	66.18	6.32	6.45	$C_{15}H_{17}N_3O_2$
Cl	CH_3	Cl	73.9–74.9	55.75	56.07	3.96	4.19	$C_{13}H_{11}N_3Cl_2$

R_1	R_2	R_3	M.p., °C. (cor.)	Literature references
H	H	CH_3O	86.6–87.6	11, 13, 14
H	H	CH_3	86.1–86.7	10, 11
H	H	Cl	87.7–88.4	11
H	H	NO_2	148.0–148.4	11, 12
CH_3O	H	CH_3O	99.0–99.9	10
CH_3	H	CH_3	117.3–117.9	10, 11
Cl	H	Cl	129.0–129.3	11
H	CH_3	CH_3O	46.4–47.1	13
CH_3O	CH_3	H	59.8–60.2	13
Cl	CH_3	H	67.0–67.8	13

It is not possible to arrive at any conclusion regarding the actual structure of the triazenes studied, since the observed shifts of absorption with structure are too small to justify interpretation. However, it is interesting to note the N-methyl compounds, whose structures are unequivocal, have maxima (350 mμ region) which are uniformly displaced about 6 mμ toward shorter wave lengths, compared to the corresponding unmethylated compound. This may be related to the disappearance of a hydrogen bonded system.

Absorption Spectra Data.—These data were obtained on a Cary ultraviolet recording spectrophotometer. The solvent was cyclohexane, and the concentration was adjusted to give a solution with an optical density not greater than 2.5. The data so obtained are recorded in Fig. 1 and Table I.

ALBANY, CALIF.

RECEIVED APRIL 30, 1951

---

(7) A. Burawoy, *J. Chem. Soc.*, 1865 (1937).

(8) L. Hunter, *ibid.*, 320 (1937).

(9) Hartman and Dickey, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 163.

(10) Hunter, *J. Chem. Soc.*, 320 (1937).

(11) LeFevre and Vine, *ibid.*, 1805 (1937).

(12) Hlyrorsky and Shikata, *Rec. trav. chim.*, **44**, 496 (1925).

(13) Wohl, *Bull. soc. chim.*, [5] **5**, 460 (1938).

(14) Vorlander and Ritter, *Ber.*, **62B**, 2824 (1929).