

[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}

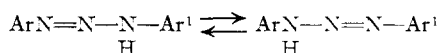
The spectra of nineteen variously substituted derivatives of 1,3-diphenyltriazene have been determined in an attempt to elucidate the problem of the structure of aromatic triazenes in solution by a study of their absorption spectra. However, no conclusive argument regarding structure can be drawn from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



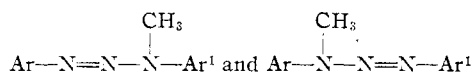
No completely satisfactory answer to the problem of the structure of these compounds either in solution or in the solid state has been presented, even though there is an extensive literature on the subject.²

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



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 dienes⁵ and carotene⁶ 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.



A series of appropriately substituted triazenes 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

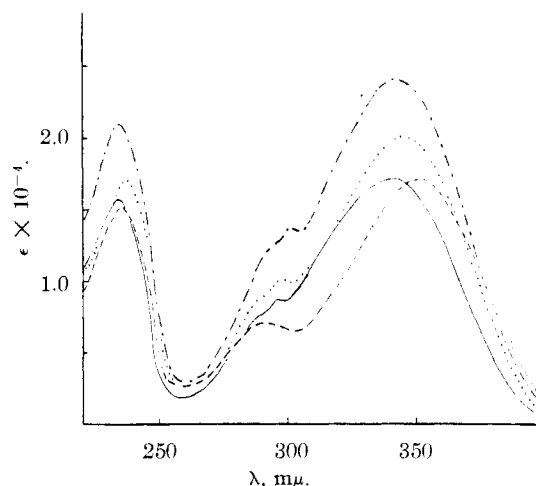


Fig. 1.—Absorption spectra of some aromatic triazenes: —, $\text{C}_6\text{H}_5\text{N}=\text{N}-\text{N}-\text{C}_6\text{H}_5$; ---, $p\text{-CH}_3\text{C}_6\text{H}_4\text{NH}-\text{N}=\text{N}-\text{C}_6\text{H}_5$; — · —, $\text{C}_6\text{H}_5\text{N}=\text{N}-\text{N}-\text{C}_6\text{H}_5\text{CH}_3\text{-}p$; · · · · ·, $p\text{-CH}_3\text{C}_6\text{H}_4\text{N}=\text{N}-\text{N}-\text{C}_6\text{H}_5\text{CH}_3\text{-}p$.

TABLE I
ABSORPTION MAXIMA FOR VARIOUS TRIAZENES

$\text{R}_1-\text{C}_6\text{H}_4-\text{N}=\text{N}-\underset{\text{R}_2}{\text{N}}-\text{C}_6\text{H}_4-\text{R}_3$			1st maximum		2nd maximum		3rd maximum	
R_1	Compound R_2	R_2	$m\mu$	$\epsilon \times 10^{-4}$	$m\mu$	$\epsilon \times 10^{-4}$	$m\mu$	$\epsilon \times 10^{-4}$
H	H	H	346	1.82	287	0.77	238	1.80
					293	0.77		
$\text{CH}_3\text{O-}$	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	1.60
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_3	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	$\text{CH}_3\text{O-}$	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 $m\mu$. The latter two bands are presumably the bands characteristic of aromatic amines, somewhat intensified and altered by substitution of the N-aryazo group. This similarity can be seen more clearly by an examination of the data in Table II. The band at about 350 $m\mu$ 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).

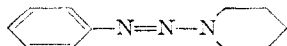
(5) Y. Hirshberg, E. Bergmann and F. Bergmann, *ibid.*, **72**, 5720 (1950).

(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--NH₂

R	λ (m μ)	ϵ	Maxima λ (m μ)	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 maximum⁷ 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}

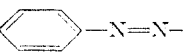
Experimental Part

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 (Harsco), 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 R₁--R₂

R ₁	R ₂	R ₃	M.p., °C. (cor.)	Analyses, %				Empirical formula
				Carbon		Hydrogen		
				Calcd.	Found	Calcd.	Found	
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 ₃ F ₃
CF ₃	H	–CF ₃	119.1–119.3	50.46	50.59	2.72	2.88	C ₁₄ H ₉ N ₃ F ₅
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 ₃ Cl
CF ₃	CH ₃	H	86.0–86.9	60.21	59.97	4.33	4.39	C ₁₄ H ₁₂ N ₃ F ₃
H	CH ₃	H	Oil	73.91	73.88	6.20	6.31	C ₁₃ H ₁₂ 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 ₃ O–	CH ₃	CH ₃ O–	103–103.9	66.40	66.18	6.32	6.45	C ₁₅ H ₁₇ N ₃ O ₂
Cl	CH ₃	Cl	73.9–74.9	55.75	56.07	3.96	4.19	C ₁₃ H ₁₁ N ₃ Cl ₂
Literature references								
H	H	CH ₃ O	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 ₃ O	H	CH ₃ O	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 ₃ O	46.4–47.1	13				
CH ₃ O	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 m μ region) which are uniformly displaced about 6 m μ toward shorter wave lengths, compared to the corresponding unmethylated compound. This may be related to the disappearance of a hydrogen bonded system.

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

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

- (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) Hlyorsky and Shikata, *Rec. trav. chim.*, **44**, 496 (1925).
- (13) Wohl, *Bull. soc. chim.*, [5] **6**, 460 (1938).
- (14) Vorlander and Ritter, *Ber.*, **62B**, 2824 (1929).