15. Electronic Absorption and Emission Spectra of 1,3-Diaryltriazenes[1]

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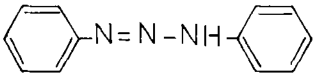
Summary

The *Pariser-Parr-Pople* (PPP) type LCI-SCF-MO calculations were used to study the models of 1,3-diphenyltriazene (**1**), 1,3-bis(3-pyridyl)triazene (**2**), 1,3-bis(2,4-dichlorophenyl)triazene (**3**), and 1,3-bis(4-ethoxycarbonyl)triazene (**4**). The results of the calculations were compared with the experimental electronic absorption and emission (fluorescence, phosphorescence) spectra of these compounds.

Introduction. – In several previously published papers on triazenes, electronic spectra were utilized to study their tautomeric structures [1–6]. Our interest in the photochemical behavior of 1,3-diaryltriazenes [7] [8] has prompted us to investigate their electronic absorption and emission spectra and to compare the experimental results with the calculated transitions obtained by using the PPP (*Pariser-Parr-Pople*, LCI-SCF-MO) method. The four compounds selected for this study were 1,3-diphenyltriazene (diazoaminobenzene) (**1**), 1,3-bis(3-pyridyl)triazene (**2**), 1,3-bis(2,4-dichlorophenyl)triazene (**3**), and 1,3-bis(4-ethoxycarbonyl)triazene (**4**).



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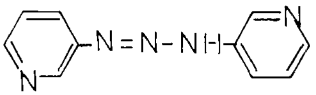

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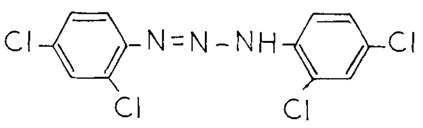

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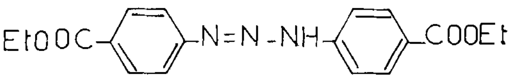

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The formerly reported calculations on 1-phenyl-3,3-dimethyltriazenes used the HMO method [9]. Also, models of a series of heterocyclic unsymmetrical triazenes were successfully treated by the PPP method [10].

Results and Discussion. - The experimental electronic absorption and emission spectra of 1,3-diphenyltriazene (**1**) in methanol are shown in the *Figure* and the experimental absorption bands of triazenes and their intensities are compared with the calculated data in *Table 1.*

The emission characteristics of compounds **1**-**4** are summarized in *Table 2* along with their calculated S_1 and T_1 energies.

Electronic absorption spectra of the compounds **1**-**4** contain three intense absorption bands. The longest-wavelength absorption band (at about 360 nm) can be associated with the presence of the $-N{=}N-$ chromophore, whereas the two remaining bands (at ~290 and ~240 nm) are those normally present in aromatic amines. The bands do not possess any pronounced fine structure.

It can be seen from the *Figure* and *Table 1* that there is generally a good agreement between the experimental absorption curves and the calculated transitions (*cf.* also [10]).

Table 1. *Electronic absorption spectra of 1,3-diaryltriazenes* (in methanol)

No.	Compound	Experimental		Calculated	
		$\tilde{\nu}_{max}$ [kK]	log ε	$\tilde{\nu}_{max}$ [kK]	log f a)
1	1,3-Diphenyltriazene	28.16	4.199	28.62	0.149
		34.72	3.703	34.97	−1.892
				35.21	−3.670
		42.02	3.952	42.23	−0.978
				42.87	−1.426
2	1,3-Bis(3-pyridyl)triazene	28.25	4.200	28.45	0.150
				33.80	−1.865
		34.13	3.968		
				35.59	−0.974
		40.81sh	3.490	41.79	−1.679
				42.32	−1.424
		43.85	3.649	44.01	−0.339
3	1,3-Bis(2,4-dichlorophenyl)triazene	27.55	4.331	28.41	0.153
		32.79	4.012	34.70	−1.744
				35.07	−2.596
		40.65	4.155	41.81	−1.262
				42.65	−1.209
				43.13	−0.446
4	1,3-Bis(4-ethoxycarbonyl)triazene	26.74	4.459	26.68	0.187
		34.12 b)		36.26	−1.177
		34.25 b)		37.52	−0.150
				38.39	−0.908
		39.22	3.646	39.28	−0.869

a) log f + 4 ≙ log ε.

b) Poorly resolved.

Table 2. *Fluorescence and phosphorescence of 1,3-diaryltriazenes* (EPA, 77 °K)

No.	Compound	Experimental[a]		Intensity phosphorescence/ fluorescence	Calculated			τ[b] [s]
		S_1[c]	T_1		S_1	T_1	T_1[d]	
1	1,3-Diphenyltriazene	85.0 (80.5)	71.6	> 20	81.8	42.9	65.2	1.5 ±0.5
2	1,3-Bis(3-pyridyl)triazene	78.5 (80.7)	64.3	~ 10	81.3	42.5	64.6	2.0 ±0.5
3	1,3-Bis(2,4-dichlorophenyl)triazene	78.5 (78.7)	65.1	≫ 100	81.2	43.0	65.4	0.20±0.05
4	1,3-Bis(4-ethoxycarbonyl)triazene	78.3 (76.4)	64.2	-	76.2	41.4	62.9	2.5 ±0.5

[a] In kcal/mol.

[b] Triplet lifetime.

[c] Values without parentheses from fluorescence spectra, values in parentheses from absorption spectra.

[d] T_1 (corr.) = 1.52 T_1.

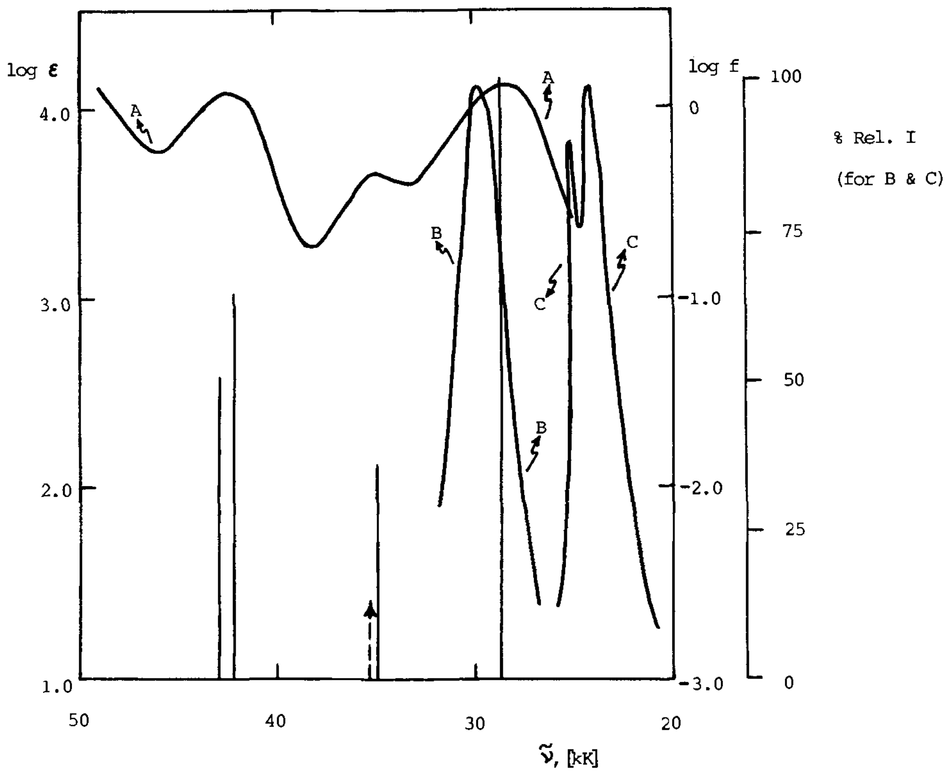


Figure. *Electronic absorption and emission spectra of 1,3-diphenyltriazene* (**1**). - *A* Electronic absorption spectrum in methanol. Calculated LCI transition energies and intensities are shown as full straight lines. The scale for the calculated oscillator strength is shown on the right-hand side. The broken-line arrow indicates a forbidden transition. - *B* Fluorescence spectrum in EPA at 77 °K. - *C* Phosphorescence spectrum in EPA at 77 °K.

1,3-Diphenyltriazene (**1**) exhibits an unusual blue shift of the fluorescence peak relative to the first absorption peak. This discrepancy is not observed with other compounds under study. The two measurements (absorption and fluorescence) were taken at two different temperatures and in two different solvents which could account for the shift. Another possibility is that absorption occurs from a higher vibrational level of the ground state.

In the case of the phosphorescence emission spectra *(Table 2)* the calculated T_1 energies are too low. This is not surprising and it is due to the deficiency of the *Mataga* parameters. If the calculated triplet energies are multiplied by an empirical correction factor of 1.52, a satisfactory agreement is obtained.

The results of the present study make it possible to conclude that both the S_1 and T_1 states of the triazenes under study are π,π^*-states. The electronic absorption and fluorescence spectra do not possess any fine structure and the intensity of the $S_0 \rightarrow S_1$ absorption band is high ($\varepsilon \sim 20{,}000$). In general, the triplet-state lifetimes of the triazenes are longer than 1 s, with the exception of the tetrachlorosubstituted compound **3**. Although the phosphorescence to fluorescence ratio is much higher in **3** than in **1**, the triplet lifetimes of **3** is almost an order of magnitude shorter. This is undoubtedly due to the heavy atom effect. Finally, the difference between the S_1 and T_1 energies is larger than 8.5 kcal/mol.

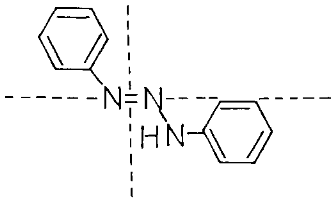
It is not possible to decide on the basis of the above results whether the photolysis of triazenes occurs from the S_1 or the T_1 state [7] [8].

Experimental Part

Compounds. The synthesis of compounds **1-4** and the determination of their purity (thin-layer chromatography) have been reported elsewhere [11] [12].

Spectra. The electronic absorption spectra of the compounds under study were measured in methanol on a *Cary* 14 spectrophotometer. The fluorescence and phosphorescence emission spectra of the triazenes were recorded in *EPA* at 77°K. The emission measurements were carried out with an *Aminco-Bowman* spectrophotofluorometer equipped with *Aminco-Keirs* phosphoroscope accessory. The fluorescence of these compounds was too weak at room temperature to be measurable.

PPP (LCI-SCF-MO) treatment. The calculations were performed on an *IBM* 360/65 computer using the usual version of the PPP method. The parameterization and the method have been described elsewhere [13] [14]. SCF-MO's served as the basis for CI. calculations. Only resonance integrals between nearest neighbors were considered. Interactions between singly excited configurations formed by promotion of one electron from one of the four highest occupied MO's to one of the four lowest unoccupied MO's were considered (our previous experience indicates that this extent of configuration interaction is usually sufficient for satisfactory results). The triazenes studied were assumed to be *trans* and planar, with idealized geometry (regular hexagons, all bond lengths 1.40 Å except for the Cl-atom and COOEt substituents).



The parameters used in calculations are summarized in *Table 3* [15–18].

I_μ and A_μ are the ionization potential and electron affinity of atom μ in the atomic valence state, respectively. The monocentric electronic repulsion integrals and core integrals between nearest neighbors are represented by $\gamma_{\mu\mu}$ and $\beta_{C-\mu}$, respectively, and Z_μ is the core charge at atom μ. The bicentric electronic repulsion integrals have been calculated using the *Mataga-Nishimoto* formula [19]

$$\gamma_{\mu\nu} = \frac{14.399}{R_{\mu\nu}+1.328}\ \mathrm{eV},$$

where $R_{\mu\nu}$ (Å) is the distance between atoms μ and ν.

Table 3. *Parameters used in the PPP treatment* (in eV)

Atom (μ)	I_μ	A_μ	$\gamma_{\mu\mu}$	Z_μ	$\beta_{C-\mu}$	$l_{C-\mu}$, Å
C	11.22	0.69	10.53	1	−2.318	1.40
N (–N=)	14.10	1.80	12.30	1	−2.318[a])	1.40[a])
N (–NH–)	23.13	10.15	12.98	2	−2.550[b])	1.40[b])
Cl	25.07	13.80	11.27	2	−0.927	1.70
O (C=O)	16.10	2.10	14.00	1	−2.300	1.23
O (OEt)	33.80	10.80	23.00	2	−2.100	1.36

[a]) $\beta_{N=N}$ −2.318, $l_{N=N}$ 1.40.
[b]) β_{N-N} −2.930, l_{N-N} 1.40.

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