

π -ELECTRONIC STRUCTURE AND CHARGE-TRANSFER SPECTRA
OF π -COMPLEXES OF MONOSUBSTITUTED
1-PHENYL-3,3-DIMETHYLTRIAZENES*

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Received July 10th, 1975

π -Electronic structure of a series of substituted 1-phenyl-3,3-dimethyltriazenes ($-\text{F}$, $-\text{Cl}$, $-\text{Br}$, $-\text{I}$, $-\text{CHO}$, $-\text{CN}$, $-\text{OH}$, $-\text{NH}_2$, $-\text{N}(\text{CH}_3)_2$, $-\text{NO}_2$, $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{COOH}$, $-\text{COOCH}_3$, $-\text{CONH}_2$, $-\text{NHCOCH}_3$) is discussed on the basis of HMO calculations especially with respect to π -electron density distribution.

Charge-transfer spectra of π -complexes of the substituted triazenes with chloranil have been measured. The experimental results have been correlated with energies of the highest occupied molecular orbital of the triazenes, and the dependence has been found to be split into two parts according to the type of substituent.

In the π -electronic approximation the donor ability of conjugated compounds can be described by energy of the highest occupied π molecular orbital (HOMO). Experimentally it is possible, in the case of compounds forming a homogeneous series with respect to their structure, to determine relative energies of the first charge-transfer bands of their π -complexes with a suitable π -electronic acceptor. In the case of a triazene the information of their ability is important, because frequently the charge-transfer interaction forms a type of primary attack of the organic compounds with a biological substrate.

In connection with the study of π -electronic structure and properties of 1-phenyl-3,3-dimethyltriazene and its derivatives, this paper deals with interpretation of their charge-transfer spectra with various π -acceptors.

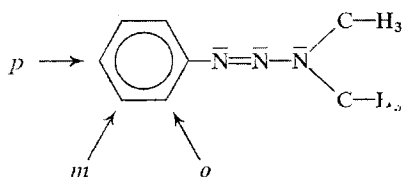
EXPERIMENTAL

The used substituted triazenes were prepared by the methods described in refs^{1,2} which give also their physical constants. The chloranil was of *p.a.* purity grade. The charge-transfer spectra of π -complexes were measured with a Perkin-Elmer 356 spectrophotometer in dichloromethane by the standard method. Formation of a sufficient concentration of the complex necessitated a 50–100 fold excess of the donor; the chloranil solution was about 10^{-3}M .

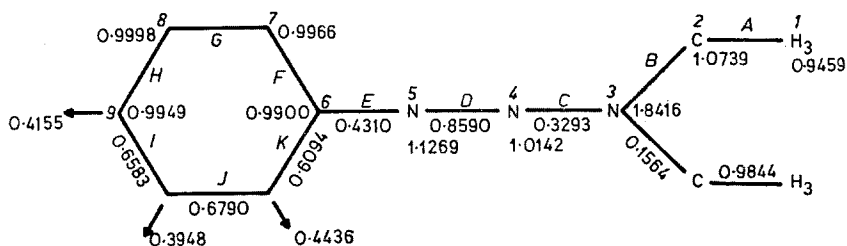
* Part VIII in the series 1-Aryl-3,3-dialkyltriazene Compounds; Part VII This Journal 37, 839 (1972).

THEORETICAL

In the ground state of the non-substituted molecule of 1-phenyl-3,3-dimethyltriazene (further only triazene) it is possible to differentiate two groups of conjugated atoms: a triazene bridge resp. dimethyltriazene bridge and an in some way disturbed benzene nucleus. Structure of the triazene (as *e.g.* from X-ray or electron diffraction) is not known. The HMO calculations were carried out with the parameters given in Table I and indicating that a rather classical structure of the parent system was presumed (Scheme 1; the arrows show the substitution positions). The mentioned calculations gave the values of π -electronic bond orders $p_{\mu\nu}$, π -electronic densities q_{μ} and free valences F_{μ} ; these values are given in molecular diagram for the ground state of the non-substituted triazene (Scheme 2), the data for the other substances being available in the laboratories of the authors of the present paper.



SCHEME 1



SCHEME 2

RESULTS AND DISCUSSION

From the π -electron density values at individual centres in molecular diagram of the non-substituted triazene it is obvious that the disturbed benzene nucleus — all of its six carbon atoms — has a slight positive charge, positive charge being also at amino nitrogen (3) of triazene bridge; the both pyridine type nitrogens forming a sort of azo group have negative charge; this charge is markedly smaller at the nitrogen (4) bound to more electron-attracting amino nitrogen than at the nitrogen (5) bound

to benzene nucleus. For comparison of the substituent effect on the two methyl groups bound to the amino nitrogen we state that on the basis of our HMO calculation the methyl carbon carries a negative charge, whereas the pseudoatom H_3 has a positive charge, the difference with respect to unity being, of course, smaller than it would correspond to the negative increase at the methyl carbon atom. The hyperconjugation model of this group thus causes conjugation (even if a slight one) with the main conjugated parts of the molecule resulting in the negative charge transfer to the carbon atoms of the both methyl groups.

TABLE I
Empirical Parameters^a HMO

Atomic core X	Z_μ	δ_X	k_{X-Y}	X—Y bond
C ⁺ (aromatic)	1	0	1	C=C
N ⁺ (pyridine)	1	0.5	1	$\text{>C}-\bar{N}=\bar{N}$
			1.1	$-\bar{N}=\bar{N}-$
N ²⁺ (amino)	2	1.5	0.7	$=\bar{N}-\bar{N}<$
			0.8	$>\bar{N}-\text{CH}_3$
C ⁺ (methyl)	1	0	0.8	$\text{H}_3\text{C}-\bar{N}<$
H ₃ ⁺ (pseudoatom)	1	-0.5	3	C—H ₃
F ²⁺	2	3.0	0.7	F—C
Cl ²⁺	2	2.0	0.4	Cl—C
Br ²⁺	2	1.5	0.3	Br—C
I ²⁺	2	1.3	0.25	I—C
HC ⁺ (formyl)	1	0.2	1.0	OCH—C
O ⁺ (formyl)	1	2.0	1.0	O—CH
C ⁺ (cyano)	1	0.0	1.0	NC—C
N ⁺ (cyano)	1	1.0	1.0	N—C
HO ²⁺ (hydroxy)	2	2.0	0.8	HO—C
H ₂ N ²⁺ (amino)	2	1.5	0.8	H ₂ N—C
N ²⁺ (nitro)	2	2.0	0.8	O ₂ N—C
O ⁺ (nitro)	1	1.0	0.7	O—N
C ⁺ (methyl)	1	0.0	0.8	H ₃ C—C
O ²⁺ (methoxy)	2	2.0	0.8	H ₃ CO—C
			0.8	H ₃ C—O
C ⁺ (carboxy)	1	0.0	1.0	HOOC—C
O ⁺ (carboxy)	1	1.0	1.0	HOC=O
O ²⁺ (carboxy)	2	2.0	0.8	HO—CO
H ₂ N ²⁺ (carboxamide)	2	1.5	0.8	H ₂ N—CO
H ₃ C ⁺ (acetamino)	1	0.0	0.8	H ₃ C—CO
C ⁺ (acetamino)	1	-0.1	0.8	H ₃ COC—NH

^a $\alpha_X = \alpha_C + \delta_X \beta_{CC}$; $\beta_{X-Y} = k_{X-Y} \beta_{CC}$.

From the point of view of the π electron bond orders $p_{\mu\nu}$, the benzene nucleus of the ground state of this non-substituted system appear as very slightly disturbed (see also the almost unity value of π electron density), because G, H, I, J are almost aromatic bonds, and only F and K have slightly more single bond character. The double bond character between the nitrogens (5) and (4) of the triazene bridge corresponds roughly to an azo group double bond; the bonds between the tertiary ring carbon atom and nitrogen (5) and between the nitrogens (4) and (3) have a considerably single character, the latter bond being more single due to higher electro-negativity of amino nitrogen atom. The bond between the amino nitrogen (3) and carbon of the methyl group have the most single character of the whole studied system, which indicates that the substituents at the phenyl group will affect but slightly the both methyl groups.

Influence of five chosen substituents ($-\text{Cl}$, $-\text{CH}_3$, $-\text{OCH}_3$, $-\text{COOCH}_3$ and $-\text{CONH}_2$) at all three ring positions of the π electron structure of these molecules indicates that the values of bond orders of the parent skeleton are not fundamentally influenced by substitution, so that the geometry of this skeleton is the same in the ground states of monosubstituted and non-substituted 1-phenyl-3,3-dimethyltriazenes. π -Electron structure (values of π -electron bond orders and π -electron densities) of the both methyl groups is identical even in the case when the molecule does not have in the HMO approximation the symmetry of the point group C_{2v} ; dependence of π -electron structure of methyl group on the type of substituent and its position is slight, the same being true for the π -electron structure of individual substituents.

We have already mentioned that all six centres of benzene ring of non-substituted triazene have positive charges. In the case of the above five chosen substituents it can be generally stated that for all three substituent positions there can be observed alternation of π electron charge in the benzene nucleus, the polarity of the centres being equal for *ortho* and *para* isomer only in the case of positive substituents $-\text{CH}_3$ and $-\text{OCH}_3$; in the case of substitution at *meta* position by the substituents $-\text{CH}_3$ and $-\text{OCH}_3$ there occurs a change of polarity of the centres with respect to *ortho* and *para* position isomers. In the case of the substituent $-\text{Cl}$ it is not possible to find such an unambiguous relation between individual position isomers, and this substituent gives such a polarity of the centres which is exhibited by negative substituents $-\text{COOCH}_3$ and $-\text{CONH}_2$. Hence from the point of view of π -electron charge distribution in the benzene ring it is possible to differentiate between three types of substituents: 1) $-\text{CH}_3$, $-\text{OCH}_3$; 2) $-\text{Cl}$; 3) $-\text{COOCH}_3$ and $-\text{CONH}_2$.

Similar analysis from molecular diagrams can be carried out also for the atoms and bonds of triazene bridge. In the triazene molecule both the triazene bridge and benzene ring are sites of π electron charge. From the algebraic sum of the relative charges it can be deduced that $-\text{OCH}_3$ group supplies electrons to all three positions about 10 times as willingly as $-\text{CH}_3$ group, whereas $-\text{Cl}$ group is only twice as efficient. The negative groups $-\text{COOCH}_3$ and $-\text{CONH}_2$ withdraw π electrons

from all positions of the conjugated system approximately to the same extent (effect of $-\text{COOCH}_3$ group is somewhat stronger).

Chloranil turned out to be the most suitable acceptor for studying charge-transfer spectra of triazenes (complexes with tetracyanoethylene are labile as in the case of some aromatic amines and aza analogues of aromatic hydrocarbons^{3,4}; complexes with 1,3,5-trinitrobenzene are little coloured). With triazenes it forms coloured complexes with typical broad charge-transfer band. Fig. 1 gives the dependence of HOMO energy (in β units) on wave number of charge-transfer bands of π -complexes of the systems studied (Table II; the values accompanying the data of maxima express the relative inaccuracy of their determination with respect to great breadth of the charge-transfer bands; in Fig. 1 this fact is expressed by the length of line). As in the case of other correlations between physico-chemical properties or reactivity and theoretical HMO data, in our case the results split into two partial dependences. The correlation parameters of the respective dependences were calculated by the least squares method. If the splitting of data is not considered, a not very close correlation I is obtained (corr. coeff. = 0.86). From the Figure it is obvious that it is better to take into account the splitting of data into partial dependences. The correlation II (corr. coeff. = 0.90) involves the non-substituted triazene and the positively substituted triazenes. The still better correlation III (corr. coeff. = 0.99) is obtained on excluding from the dependence the non-substituted and *m*-methoxy triazenes. The correlation IV is relatively very close, too (corr. coeff. = 0.95); it involves the halogen-derivatives and negatively substituted triazenes. Passing from the correlation

TABLE II

Wave Numbers of Charge-Transfer Bands $\tilde{\nu}_{\text{CT}}$ (μm^{-1}) of π -Complexes of Triazene Derivatives with Chloranil and Energies of the Highest Occupied HMO, ϵ_{HOMO} in β Units

Molecule	<i>ortho</i>		<i>meta</i>		<i>para</i>	
	$\tilde{\nu}_{\text{CT}}$	ϵ_{HOMO}	$\tilde{\nu}_{\text{CT}}$	ϵ_{HOMO}	$\tilde{\nu}_{\text{CT}}$	ϵ_{HOMO}
Triazene	1.77	<i>h</i> 0.703				
-Cl	1.84 \pm 0.01	0.692			1.80 \pm 0.01	0.684
-Br			1.84 \pm 0.02	0.701	1.80 \pm 0.02	0.686
-I					1.79 \pm 0.01	0.687
-CH ₃	1.69 \pm 0.01	0.684	1.72 \pm 0.1	0.699	1.70 \pm 0.01	0.672
-OCH ₃	1.65 \pm 0.1	0.642	1.75 \pm 0.1	0.686	1.60 \pm 0.01	0.621
-CN					1.90 \pm 0.02	0.737
-COOCH ₃	1.96 \pm 0.02	0.719	1.85 \pm 0.01	0.707	1.91 \pm 0.01	0.734
-CHO					1.91 \pm 0.02	0.769
-CONH ₂	1.97 \pm 0.03	0.719	1.85 \pm 0.01	0.707	1.89 \pm 0.1	0.732

II to III is not chemically illogical, if we consider that the non-substituted triazene represents a transition between positively and negatively substituted derivatives, and that *m*-methoxy derivative forms an exception with respect to electronic structure and properties (*cf.* its anomalous position in the Hammett σ constants scale). The triazenes carrying *o*-COOCH₃ and *o*-CONH₂ groups deviate from the above dependences, too. On the basis of these two data it cannot be univocally stated if the matter is in a further partial dependence due to sterical effect of the bulky *ortho* substituents or in the non-bonding interactions between these substituents and triazene bridge or in a different structure of the π -complexes. On the basis of the calotte models these two derivatives can be considered planar to considerable extent, too, the rotation of the substituents being, however, hindered. Hence it can be stated that the data split into two partial dependences: triazenes with positive substituents and those carrying negative substituents or halogens, the non-substituted and *m*-methoxy triazenes forming a transition between the both dependences. It must be emphasized that the observed splitting is considerably smaller than that of the charge-transfer bands of π -complexes of various conjugated hydrocarbons⁵, being about 1000 cm⁻¹ in the case of the positively and the negatively charged triazenes and about 5000 cm⁻¹ in the case of aromatic hydrocarbons and polyenes. The marked splitting of data in the case of conjugated hydrocarbons is ascribed to different structure of complexes due to very different magnitude of polynuclear aromatic hydrocarbons *vs* long systems of polyenes. Analogous explanation offers in triazene series. Unfortunately there are no data concerning structure of their π -complexes. However, on the basis of HMO model a simplified statement can be made about mutual orientation of the donor and the acceptor. Fig. 2 denotes the nodal planes in LFMO acceptor (chloranil) and in HOMO of some *o*-, *m*- and *p*-substituted tria-

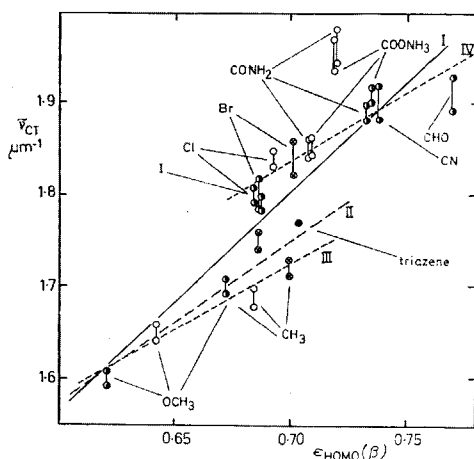


FIG. 1

Dependence of HOMO Energy (in β units) on Wave Number of Charge-Transfer Bands of π -Complexes of the Studied Systems with Chloranil

○ *ortho*-, ⊗ *meta*- and ● *para*-isomers.

zenes. The nature and position of substituent has no effect on the shape of HOMO of triazene skeleton of all the systems studied. From the shape of frontier orbitals of the partners in the π -complex it can be deduced that all the studied π -complexes of triazenes with chloranil have approximately the same structure, *viz.* the sandwich arrangement where the six-membered rings of the both partners are more or less one above the other. Hence it is likely that the splitting of data is not due to different structure of the complex. Neither is it due to solvent effect. We have found that solvent has practically no effect on position of the charge-transfer bands of vari-

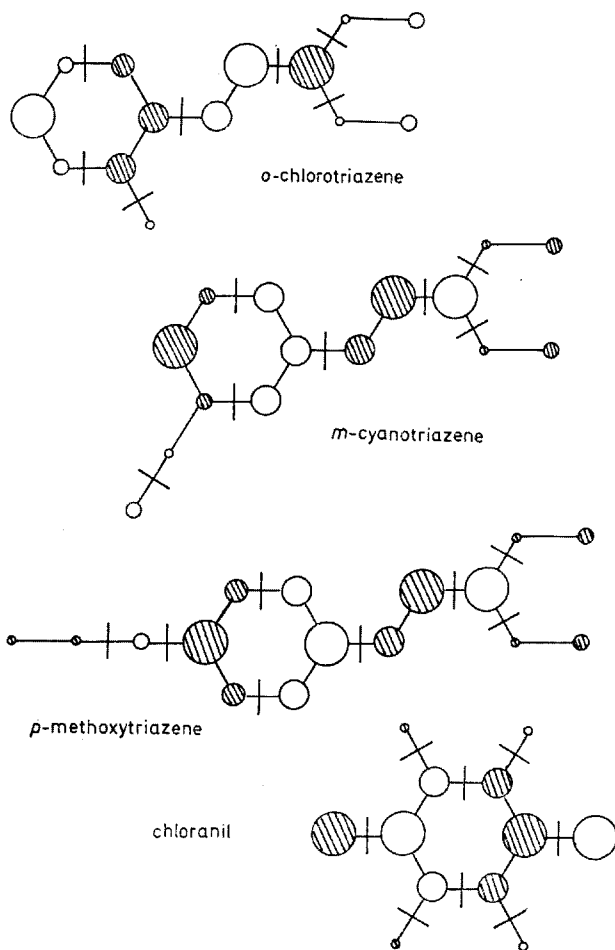


FIG. 2

Graphical Illustration of LUMO of Chloranil Molecule and of HOMO of Some *o*-, *m*- and *p*-Substituted Triazenes

ous substituted triazenes (the solvents used were hexane, cyclohexane, dichloromethane, chloroform, tetrachloromethane). Hence the reason of the splitting of data must be seen in the simplicity of the used theoretical model and its application on complex systems with several different heteroatoms. In this respect the obtained good correlation of partial dependences is certainly remarkable and forms a further backing for applicability of the HMO method even in such cases like the present series; the condition must, of course, be strictly observed that the compounds involved are structural relatives.

The obtained relatively good correlation between the wave number of the first absorption band of CT complex of substituted triazenes and the corresponding eigenvalue of the highest occupied HMO, ϵ_{HOMO} , is not surprising; it is, however, very surprising that the dependence is split into two partial dependences, with much closer correlation, according to the type of substituent and not to its position. We found⁶ that there is a good correlation between energy of CT bands of π -complexes and N-basicity (protonation constant) *i.e.* correlation between two experimental values, one of them being connected with the whole molecule, whereas the other is more or less local matter. Due to this fact we tried to find a quantum chemical index which would give a good correlation dependence with ϵ_{HOMO} which represents the quantity characterizing the donor ability of the mentioned molecules. There was,

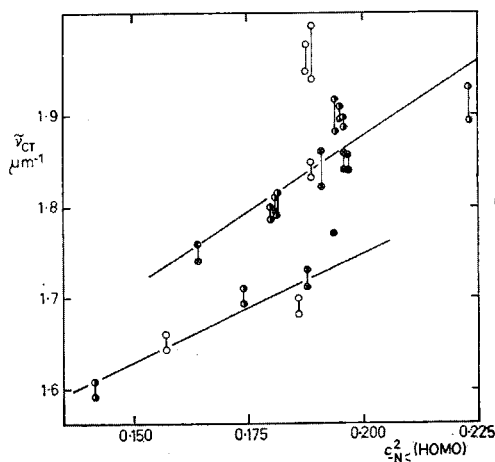


FIG. 3

Dependence of $c^2_{N<}(\text{HOMO})$ on Wave Number of Charge-Transfer Bands of π -Complexes of the Studied Systems with Chloranil

○ *ortho*-, ⊗ *meta*- and ● *para*-isomers.

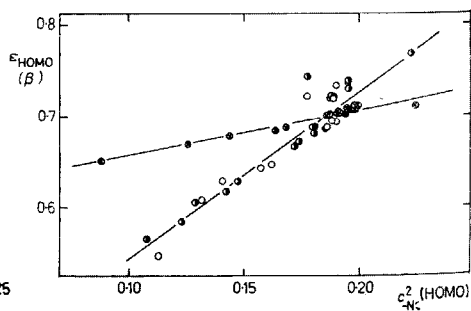


FIG. 4

Dependence of HOMO Energy (in β units) on $c^2_{N<}(\text{HOMO})$ for Substitution Derivatives of Triazene

○ *ortho*-, ⊗ *meta*- and ● *para*-isomers.

of course, a possibility of correlation with π -electron density at amino nitrogen $\sigma_{-N<}$ which is the highest π -electron density for all substitution derivatives irrespective of the position of the substituent. However, this index is rather insensitive to the type and position of substituent and does not present any useful correlation resp. possibility of prediction. This relatively high insensitivity of π -electron density at amino nitrogen is not much surprising, if the summary character of this quantity is realized as well as its localization at the given centre (which is sufficiently isolated due to considerably single bonds to the nitrogen) and the high similarity of the compounds studied. With respect to that in the HMO scheme the theoretical equivalent of the experimental value \bar{v}_{CT} is represented by the energy of HOMO — a quantity of non-summary character — we used for the correlation another quantum chemical index *viz.* the square of the expansion coefficient at amino nitrogen in HOMO, $c_{-N<}^2$ (HOMO). In most cases this index has its maximum value at the amino nitrogen atom, too; this index gives an analogous correlation for the dependence \bar{v}_{CT} vs $c_{-N<}^2$ (HOMO) as for the dependence \bar{v}_{CT} vs ϵ_{HOMO} (Fig. 3). Dependence of ϵ_{HOMO} on this index is given in Fig. 4; this correlation shows a marked deviation of *m*-substituted compounds.

From the characteristic structure of triazenes it is obvious that the mere π -electron approximation not involving at least the effect of σ -polarization cannot reflect the real distribution of π -charges in the studied molecules (not even semiquantitatively). In spite of that we suppose that the results obtained justify the application of HMO method for qualitative prediction of some properties of these compounds.

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Translated by J. Panchartek.