

# N=N Vibrational Frequencies and Fragmentation Patterns of Substituted 1-Aryl-3,3-Dialkyl-Triazenes: Comparison with Other High-Nitrogen Compounds

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The influence of substitution pattern and electronic structure on the N=N stretching frequencies of compounds containing three to six linearly connected nitrogen atoms has been investigated by FT-IR and Raman spectroscopy. For a series of 1-phenyl-3,3-dialkyl-triazenes,  $\text{Phe-N}^1=\text{N}^2-\text{N}^3 \text{ R}_2$ , shifts in the two valence vibrations of the triazeno group are studied with respect to the type and position of substituents at the aromatic ring, and for various alkyl substituents at  $\text{N}^3$ . The  $\text{N}^1=\text{N}^2$  stretching frequency is lowered by electron-withdrawing substituents at the aromatic ring; this effect is most pronounced for para-positioned substituents. A decrease in the  $\text{N}^1=\text{N}^2$  bond order, and of the associated valence vibration, is also observed upon introduction of heavier  $\text{N}^3$ -alkyl substituents, due to an inductive effect. Changes in vibrational frequencies are correlated with characteristic fragmentation patterns in the mass spectra of these compounds, where two degradation routes subsequent to ionization at the nitrogen atoms  $\text{N}^1$  and  $\text{N}^2$  have been observed. For the investigated pentazadiene derivatives, a weaker dependence of the N=N vibrational frequencies on the substituents is found. Mass spectra are interpreted in terms of two typical fragmentation pathways, involving a McLafferty rearrangement.

Index Headings: Mass spectroscopy; Raman spectroscopy; Triazene compounds; Electronic structure.

## INTRODUCTION

In the past few years, triazenes have been intensely investigated in view of their anti-tumor activity.<sup>1-3</sup> Recently, triazenes have been used as dopants for the XeCl excimer laser ablation of nonabsorbing polymers, such as PMMA.<sup>4,5</sup> Polymerization of suitable triazene monomers yields photopolymers that have been designed for photolithographic applications.<sup>6</sup>

In an effort to elucidate the mechanism of polymer laser ablation induced by triazene dopants, the restricted rotation around the  $\text{N}^2-\text{N}^3$  bond of the triazene group ( $-\text{N}^1=\text{N}^2-\text{N}^3-$ ) has been studied by temperature-dependent NMR spectroscopy.<sup>7</sup> Photolysis quantum yields of differently substituted triazene derivatives have been determined, and have been correlated with  $\text{N}^1=\text{N}^2$  bond orders derived from semiempirical calculations.<sup>8</sup>

In this report, the vibrations of the N=N bond of the triazenes, and of compounds containing up to six linearly connected nitrogen atoms, are investigated by IR and Raman spectroscopy. For the 1-phenyl-3,3-dialkyl-triazenes, the vibrational frequencies are influenced by the type of electron-donating or withdrawing substituents

on the phenyl ring, by the position of the phenyl substituents, and by the choice of alkyl substituents at nitrogen atom  $\text{N}^3$ . The observed changes will be discussed in terms of a 1,3-dipolar resonance structure of the triazeno group and further charge delocalization into the aromatic ring, as shown in Scheme 1. Azo derivatives, a tetrazene compound, several pentazadienes, and a hexazadiene (with structural formulas as represented in Scheme 1) are included in the investigation, to confirm the trends derived from the triazene substitutions. These results are compared and correlated with relative fragment intensities derived from electron impact mass spectra.

## EXPERIMENTAL

**Materials.** The triazenes, the pentazadienes, and the hexazadiene were prepared according to the procedures described in detail elsewhere.<sup>7,9</sup>

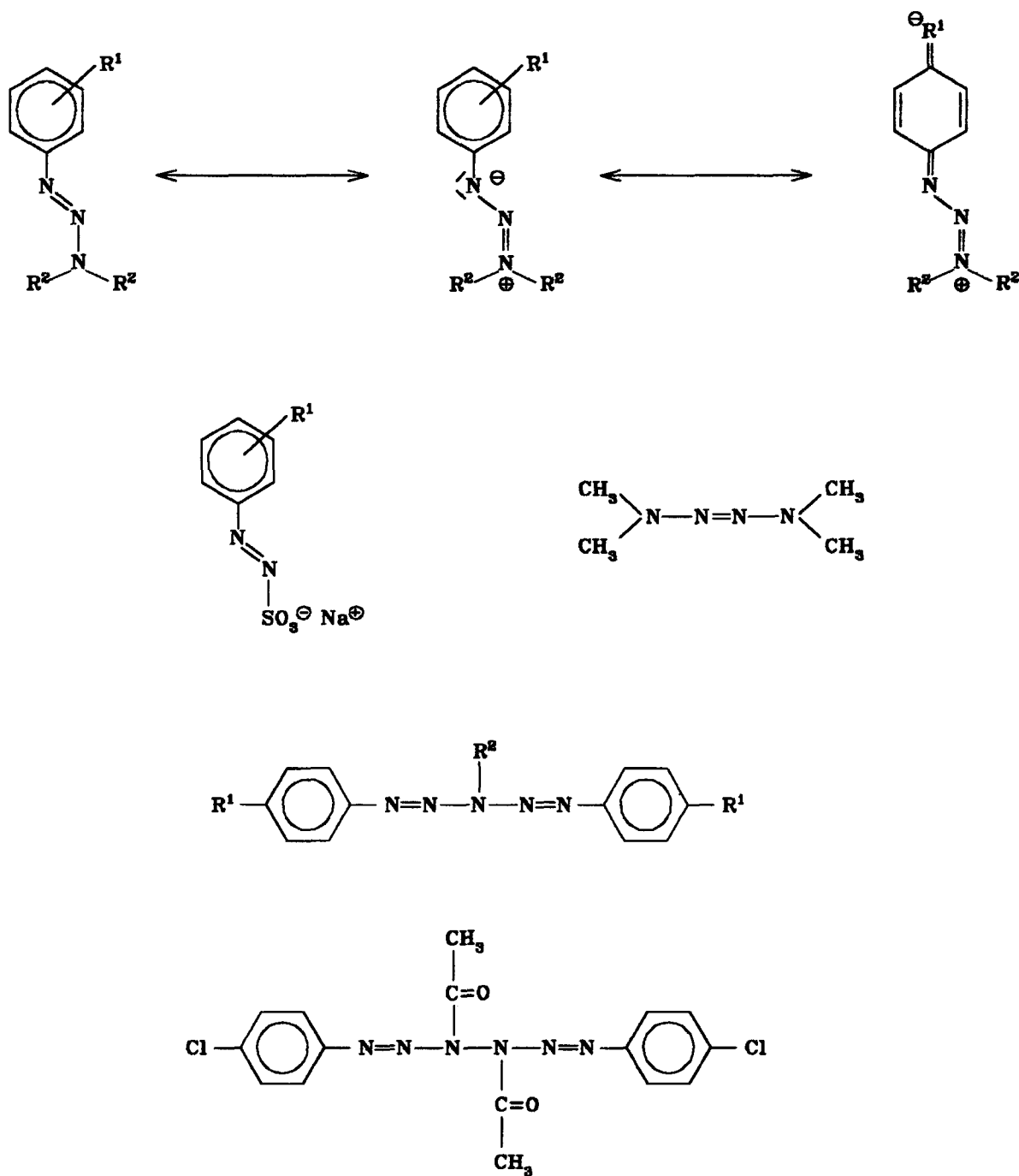
**Instruments.** Infrared spectra were recorded on an FT-IR instrument (Perkin-Elmer, Model 1710) in a diffuse reflectance cell (Spectra-Tech). Liquid substances were investigated undiluted, by placing a drop onto the reference mirror of the diffuse reflectance FT-IR (DRIFT) cell. Solid compounds were diluted by abrading the powder with a silicon carbide substrate (LOT), which was subsequently placed into the DRIFT cell. Typically, 250 scans have been coadded for each spectrum at a resolution of  $2 \text{ cm}^{-1}$ .

For Raman scattering, the pure samples were placed in quartz cuvettes, and excited with the use of either the 457.9-, 488.9-, and 514.5-nm lines of an argon-ion laser (3.9 mW to 10 mW of power), or the 476.5- and 530.9-nm lines of a krypton-ion laser (0.07 to 8 mW of power). Raman signals were dispersed in a triple spectrograph (SPEX, Model Triplemate 1877A), and detected with an optical multichannel analyzer based on a cooled photodiode array. The resolution of the triple spectrograph was set at  $7 \text{ cm}^{-1}$ ; frequency positions have been calibrated with a neon spectral lamp. The signal accumulation time on the diode array was chosen to be between 10 and 200 s, depending on laser excitation power; 10 to 20 exposures were accumulated. For some of the weaker vibrational features, the Raman spectra were deconvoluted to determine accurate band positions.

Electron impact spectra were recorded on a mass spectrometer (Finnigan, Model MAT 8500). An ionization energy of 70 eV was used; the compounds were intro-

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SCHEME 1. Investigated compounds: 1-phenyl-3,3-dialkyl-triazenes (top); azosulfonates, tetrazenes (second row); pentazadienes (third row); and hexazadienes (bottom). Dipolar resonance structures contributing to the electronic charge distribution of triazenes are indicated; the quinoid structure is possible only for acceptor substituents in the *para*-position on the phenyl ring.

duced into the instrument by a short heating period, without derivatization. After a constant ion current had been established, 10–30 spectra were averaged for recording reliable relative ion intensities (compounds 1–15).

## RESULTS

**Range of N=N Vibrational Frequencies.** The frequency of the N=N stretching vibration is found to vary over a wide area for the nitrogen compounds investigated in this study; an assignment from the IR spectrum alone is

therefore not obvious. In the Raman spectrum (cf. Figs. 1 and 2), the corresponding band is more easily recognized by its high intensity, which is due to the large polarizability derivative associated with the N=N stretch. This band is usually the most intense spectral feature. (For the *p*-nitrophenyl-diethyl-triazene, the vibration of the nitro group at  $1315\text{ cm}^{-1}$  is more intense due to the high associated Raman cross section;<sup>10</sup> note the calibration bars in Fig. 1.) Therefore, a combination of the IR and Raman spectra was used for the assignment of the N=N frequency. A survey on the N=N band positions of different nitrogen compounds is given in Table I.

TABLE I. Raman frequency ranges of N=N stretching vibrations in various classes of compounds containing nitrogen double bonds.

Compound	IR, Raman frequencies <sup>a</sup>	Source
<i>cis</i> -Azobenzene	1511	Ref. 11
<i>trans</i> -Azobenzene	1442	Ref. 11
Azosulfonates	1503-1464	Ref. 12; this work
Hexazadiene	1496	This work
Pentazadienes	1492-1441	This work
Tetrazene	1475	Ref. 13
1-Aryl-3,3-dialkyl-triazenes	1417-1372	Ref. 14; this work
1-Aryl-3-monoalkyl-triazenes	1485-1480 and 1430-1425	Ref. 14
1,3-Diphenyl-triazene	1413	Ref. 11; this work

<sup>a</sup> Measurements in  $\text{cm}^{-1}$ .

The triazenes, which exhibit the lowest N=N vibrational frequency, are known to exist in a 1,3-dipolar structure,<sup>15</sup> i.e.,  $-\text{N}^1=\text{N}^2-\text{N}^3 \leftrightarrow -\overset{-}{\text{N}}^1-\text{N}^2=\overset{+}{\text{N}}^3$ . For substituted 1-phenyl-3,3-dialkyl-triazenes, the relative importance of this structure can be correlated with the Hammett parameter  $\sigma$  characterizing the substituent on the aromatic ring. In the dipolar structure, the N=N bond is delocalized over three nitrogen atoms. This pattern gives rise to a significant red shift of the N=N stretching frequency, as compared to the other investigated nitrogen compounds.

The triazene fragment gives rise to two stretching vibrations, both of which involve all three nitrogen atoms, and couple to the vibrations of adhering substituents. The higher frequency, which we shall designate as  $\nu(\text{N}=\text{N})$  in the following discussion, has been referred to as  $\nu_{\text{as}}$  in Ref. 11. The lower frequency, designated here as  $\nu(\text{N}-\text{N})$ , was termed  $\nu_s$  in Ref. 11.

**Influence of Substituents in the *para*-Position at the Phenyl Moiety.** For the *para*-substituted compounds, the frequency  $\nu(\text{N}=\text{N})$  decreases with increasing electron-withdrawing character of the phenyl substituent. From Fig. 1 and Table II, this band is seen to vary by  $-26 \text{ cm}^{-1}$  within the set of compounds investigated. Simultaneously, the stretching frequency of the formal N-N single bond,  $\nu(\text{N}-\text{N})$ , increases to a smaller extent ( $+8 \text{ cm}^{-1}$ ). This behavior is expected for a 1,3-dipolar resonance structure. The Raman frequency of the unsubstituted compound 2 represents an exception from the sequence predicted from the inductive effects alone; the

TABLE II. Influence of substituents in *para*-position at the phenyl ring on the vibrational frequencies of the triazeno group.<sup>a</sup>

Compound	Para-substituent on phenyl ring	$\nu(\text{N}=\text{N})^b$		$\nu(\text{N}-\text{N})^b$	
		Raman	IR	Raman	IR
1	N(CH <sub>3</sub> ) <sub>2</sub>	1417/1407	1416/1406	1255	1237
2	H	1414	1414	1252	1239
3	OCH <sub>3</sub>	1408	1407	1253	1245
4	CH <sub>3</sub>	1403	1403	1254	1237
5	COOH	1397	1401	1259	1243
6	CN	1386	1384	1260 sh	1243
7	NO <sub>2</sub>	1391	1383	1259	1246

<sup>a</sup> 1-Phenyl-3,3-diethyl-triazenes.

<sup>b</sup> Measurements in  $\text{cm}^{-1}$ ;  $\nu(\text{N}=\text{N}) \equiv \nu_{\text{as}}$ ,  $\nu(\text{N}-\text{N}) \equiv \nu_s$  defined in Ref. 11.

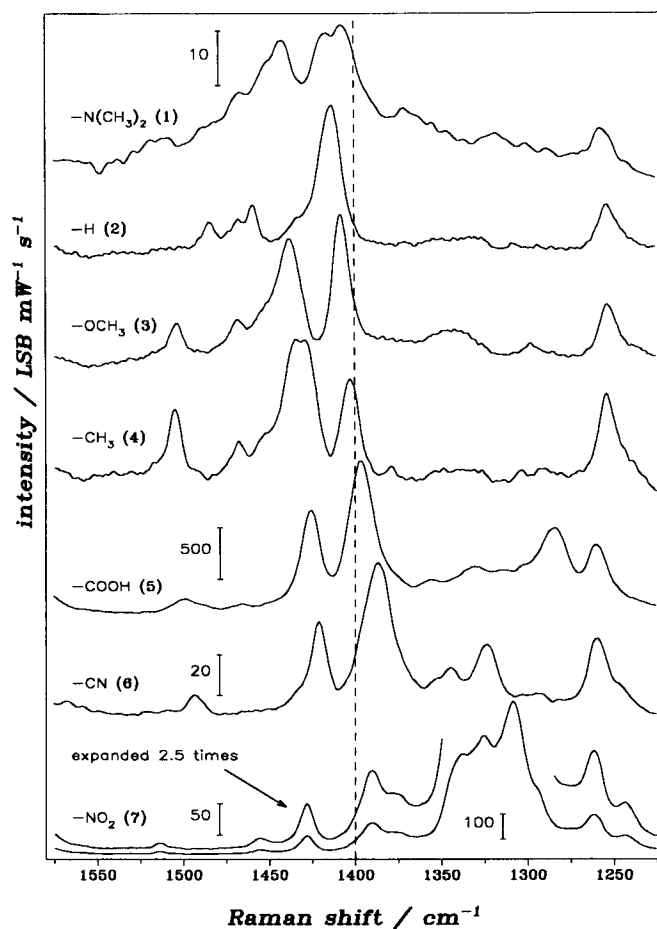


FIG. 1. Raman spectra of *para*-substituted 1-phenyl-3,3-dialkyl-triazenes. *Para*-substituents at the phenyl ring are indicated in the figure; numbers refer to Table II. Measurement conditions are mentioned in the experimental section.

higher frequency of 2 is probably due to the lower mass of the unsubstituted phenyl ring.

We note from Table II that there is close agreement in the wavenumbers of the N=N stretching frequencies derived from Raman and IR spectra. For the N-N stretch the differences are somewhat larger. Different 1-phenyl-3,3-dialkyl-triazenes are known to crystallize in the monoclinic and triclinic space groups, respectively;<sup>16,17</sup> differences in packing and interaction of the molecules could be partly responsible for the frequency shifts.

**Influence of the Position of Nitro or Carboxy Substituents on the Phenyl Ring.** Among the three 1-nitrophenyl-3,3-diethyl-triazenes, the *para*-substituted compound is characterized by the lowest value of the N=N stretching frequency (Table III). Contrary to expectation from simple resonance structure arguments, very similar frequencies are observed for the *meta*- and *ortho*-substituted derivatives. This behavior might be due to an associative bonding between the *ortho*-nitro group and the triazeno group. A related phenomenon will be discussed below in the context of fragmentation patterns observed for compound 15 in the electron impact mass spectra.

Frequencies observed with carboxy-substituents in the *meta*- and *para*-position at the phenyl ring (Table III) confirm the above interpretation: The N=N stretching

TABLE III. Influence of the position of substituents on the phenyl ring on the N=N vibrational frequencies of 1-(phenyl)-3,3-diethyl-triazenes.

Com- pound	Position and type of substituent(s)	$\nu_{as}(N=N)^a$		$\nu_s(N-N)^a$	
		Raman	IR	Raman	IR
15	2-NO <sub>2</sub>	1404	1408	1259	1238
14	3-NO <sub>2</sub>	1403	1403	1250	1241
7	4-NO <sub>2</sub>	1391	1383	1259	1246
11	3-COOH	1404	1416	1248	1245
5	4-COOH	1397	1401	1259	1243
9	3,5-COOH	1372	1386	...	1236
8	3,5-CON <sub>3</sub>	1385 (w)	1386		
		1395	1401	1243	1240

<sup>a</sup> Measurements in cm<sup>-1</sup>.

frequency of 1-(3-carboxyphenyl)-3,3-diethyl-triazene is higher by 7 cm<sup>-1</sup>, and the N-N stretch is red-shifted by 11 cm<sup>-1</sup>, as compared to the corresponding frequencies in the para-substituted derivative.

**Influence of Two Substituents in *meta*-Position at the Phenyl Moiety.** Two triazene derivatives carrying two phenyl substituents have been investigated, i.e., 1-(3,5-di-carboxyazido)-3,3-diethyl-triazene (8) and 1-(3,5-di-carboxy)-3,3-diethyl-triazene (9). Results included in Table III show that both compounds are characterized by exceedingly low values of the N=N stretching frequency. With the 3,5-dicarboxy-derivative 9, the N=N frequency (1372 cm<sup>-1</sup>, with a shoulder at 1385 cm<sup>-1</sup>), is the lowest among all investigated triazene compounds, and is very significantly red-shifted as compared to the 3-carboxyphenyl-triazene (1404 cm<sup>-1</sup>). Both the low frequency and the observed splitting in the disubstituted derivative suggest that the effects of hydrogen bonding networks are particularly pronounced for the dicarboxy compound 9, as compared to the monoacid derivatives 5 and 11.

**Influence of Alkyl Substituents at the N<sup>3</sup> Nitrogen.** Very similar vibrational frequencies have been determined for 1-(3-carboxy-phenyl)-triazenes with ethyl, *n*-propyl, or isopropyl substituents at nitrogen atom N<sup>3</sup> (Table IV). The dimethyl derivative 10 represents a remarkable exception. This triazene compound is characterized by a comparatively low activation energy of internal rotation in solution, high N<sup>1</sup>=N<sup>2</sup> bond order, and high quantum yield of photolysis.<sup>8</sup> It is therefore not clear at present why *both* stretching frequencies are lowered [ $\nu(N=N)$ : -19 cm<sup>-1</sup>;  $\nu(N-N)$ :  $\approx$  -35 cm<sup>-1</sup>] as compared to the compounds carrying heavier alkyl substituent (Table IV).

**Other Compounds Containing One or Several N=N Bonds.** Raman spectra of several pentazadiene compounds are presented in Fig. 2. In the pentazadiene func-

TABLE IV. Influence of alkyl substituents at nitrogen atom N<sup>3</sup> on the N=N vibrational frequencies of 1-(3-carboxyphenyl)-triazenes.

Com- pound	Alkyl sub- stituent	$\nu_{as}(N=N)^a$		$\nu_s(N-N)^a$	
		Raman	IR	Raman	IR
10	CH <sub>3</sub>	1385	1380	1206	1202
11	C <sub>2</sub> H <sub>5</sub>	1404	1416	1248	1245
12	<i>n</i> -C <sub>3</sub> H <sub>7</sub>	1404	1406	1230	1228
13	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	1403	1399	1250	1237
				1233 (sh)	

<sup>a</sup> Measurements in cm<sup>-1</sup>, sh = shoulder.

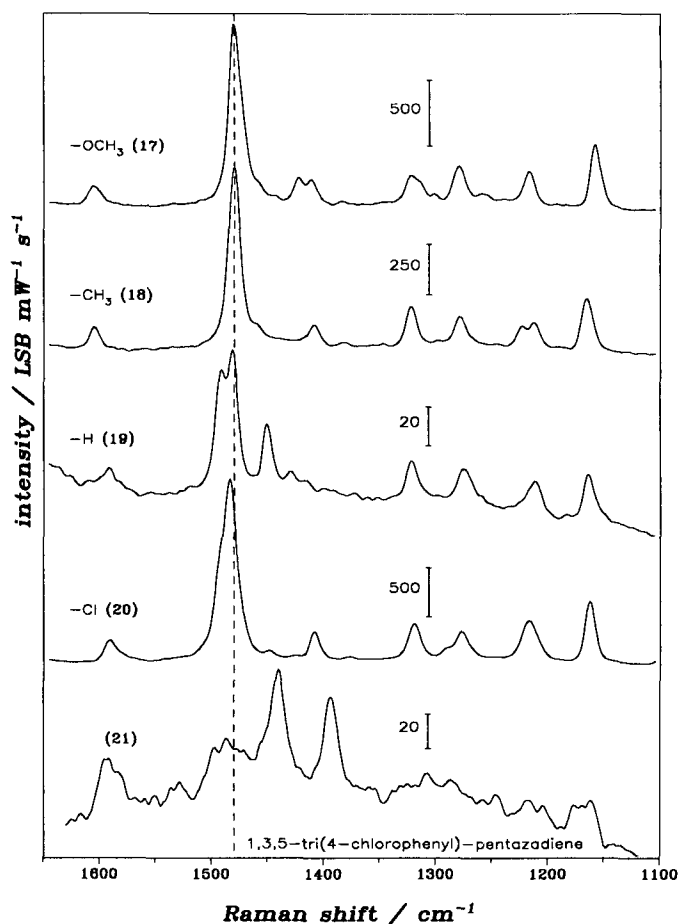


FIG. 2. Raman spectra of *para*-substituted 1,5-diphenyl-3-ethyl-pentazadienes. Substituents at the phenyl ring are indicated in the figure; numbers refer to Table V. Measurement conditions are mentioned in the experimental section.

tional group, the tendency of the central nitrogen lone pair towards delocalization is apparently less pronounced. Thus, the vibrational frequencies remain largely unchanged in the series of compounds 17 through 20 (Table V), in which the *para*-substituents of the two phenyl substituents are varied from the electron-donating methoxy group to an electronegative chloro substituent. Only for the pentazadiene 21, in which the ethyl substituent at N<sup>3</sup> is replaced by another 4-chloro-phenyl group, is a pronounced lowering of the N=N stretching frequency observed.

Similarly, the hexazadiene is characterized by a high value,  $\tilde{\nu} = 1496$  cm<sup>-1</sup>, so that delocalization of the N=N bond does not appear to be important in this compound as well. In the azo compounds and azosulfonates (Table V), no similar dipolar resonance structures are known, and the vibrational frequencies are correspondingly high.

**Electron Impact Mass Spectra.** The relative intensities of the molecular ion and of fragment ions recorded in electron impact mass spectra will be used as indicators for the stability of the respective species. Thus, the stabilizing or destabilizing effects of the various substituents are studied and correlated with the corresponding shifts of the Raman/IR frequencies.

**Mass Spectroscopic Fragmentation Patterns of Triazenes.** For the triazene compounds, a typical fragmen-

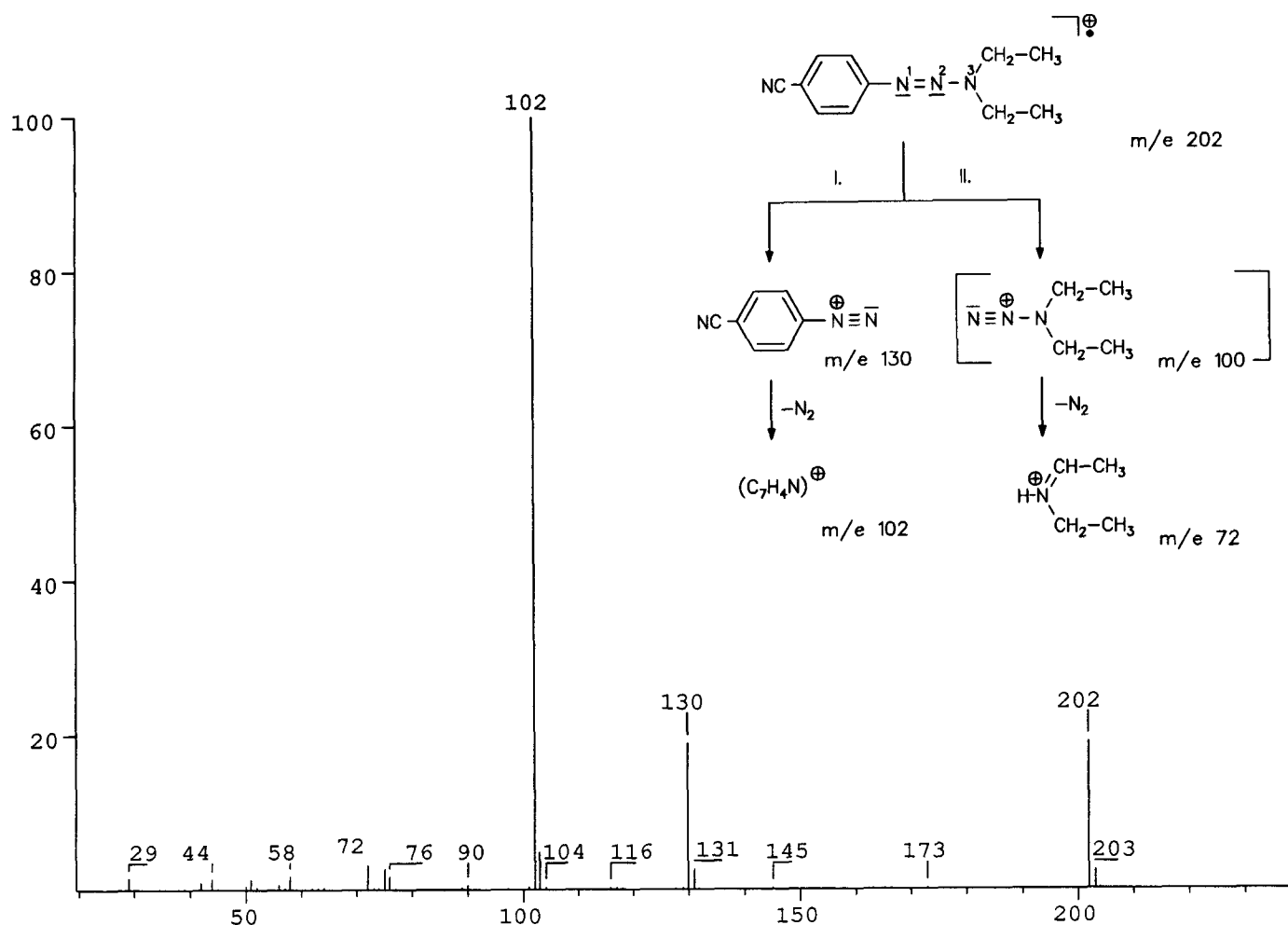


FIG. 3. Mass spectrum of 1-(4-cyanophenyl)-3,3-diethyl-triazene (compound 6). The suggested fragmentation scheme is shown as an inset.

TABLE V. N=N vibrational frequencies of other compounds containing one or several N=N bonds.

Compound	$\nu(\text{N}=\text{N})^a$	
	Raman	IR
Azo compounds		
azo benzene, <i>trans</i>	1442	
azo benzene, <i>cis</i>		1511
(2-methoxy-phenyl)-azosulfonate	1503	1498/1489
(4-methoxy-phenyl)-azosulfonate	1487	1486
	1460	1464
Tetrazene		
1,1,4,4-Tetramethyl-tetrazene	1475	...
1,5-Diphenyl-3-ethyl-pentazadienes		
phenyl substituents in 4',4''-positions:		
CH <sub>3</sub> O (17)	1480	1484
CH <sub>3</sub> (18)	1480	1478 (+shoulder)
H (19)	1492/1482	1482
Cl (20)	1484	1482 (+shoulder)
Cl <sup>b</sup> (21)	1441	1448/1442
Hexazadiene		
1,6-bis-(4-Chlorophenyl)-3,4-Diacetyl-1,5-hexazadiene (16)	1496	1496

<sup>a</sup> Measurements in cm<sup>-1</sup>.

<sup>b</sup> Substituent at nitrogen N<sup>3</sup> is 4-chlorophenyl.

tation pattern<sup>18</sup> is observed in the electron impact mass spectra, as shown for 1-(4-cyanophenyl)-3,3-diethyl-triazene (6) in Fig. 3. Ionization at N<sup>1</sup> (route I) is followed by detachment of the dialkylamino group, to produce a diazonium ion; subsequent steps are the release of nitrogen, and the eventual loss of the substituent from the phenyl ring. Ionization at the nitrogen atom N<sup>2</sup> produces the dialkylamino fragment, of lower intensity.

For a series of triazene compounds, the relative intensities of these characteristic fragments, together with those of the dialkylamino moiety, are compiled in Table VI. From the intensities of the molecular ion and of the aryl-diazonium ion—in reference to the one of the substituted phenyl fragments which consistently represents the base peak of the spectrum—a consistent trend may be derived. With increasing electron-withdrawing character of the *para*-substituents, the tendency for a cleavage of the N<sup>2</sup>-N<sup>3</sup> bond is increased, and hence the molecular ion is destabilized. This observation parallels the behavior mentioned above for the neutral parent compound; i.e., acceptor substituents in the *para*-position induce a flow of charge onto the aromatic ring, and thus increase the importance of the 1,3-dipolar resonance structure. On the other hand, with electron-donating substituents, no accommodation of the negative charge on the phenyl ring is possible; this pattern is paralleled by the comparatively high stability of the molecular ion.

Exceptions from this sequence are triazenes **2** and **4** for which the molecular ion intensities are low; these compounds do not carry substituents containing heteroatoms. Thus it appears that ionization at the hetero-atom of the phenyl substituent is another way to produce a comparatively stable molecular ion. In particular, ionization at a nitro group is a well-known process;<sup>19</sup> compound **7** does in fact display a very intense molecular ion peak. For the unsubstituted phenyl (**2**) and the methyl-substituted derivative (**4**), this possibility does not exist, and hence the molecular ion peak is weaker.

With the 1-(3-carboxyphenyl)-dialkyl-triazene compounds **10** through **13**, the relative intensities of molecular and diazonium ions decrease with increasing size of the alkyl groups. The higher  $\sigma$ -electron-donating effect (+I inductive effect) of  $-\text{C}_2\text{H}_5$  and  $-\text{C}_3\text{H}_7$ , as compared to the one of a methyl group, results in a higher probability of  $\text{N}^2\text{-N}^3$  bond breaking, and hence in the lower stability of the molecular ion. This behavior is consistent with the barriers of internal rotation and the  $\text{N}=\text{N}$  bond orders derived from earlier studies.<sup>7,8</sup> The lower the mass of the  $-\text{NR}_2$  rotor, the faster the internal rotation.

With the *ortho*-substituted nitro compound **15**, fragmentation proceeds via a different route. Ionization at the nitro group is followed by the loss of the dialkylamino substituent from the molecular ion. In this fragment ( $m/e = 150$ ), a six-membered ring involving the *ortho*-nitro substituent and nitrogen atoms  $\text{N}^1, \text{N}^2$  from the triazeno group may be formed.<sup>19-21</sup> This ring closure is suggested by the fact that *no* loss of nitrogen is observed from the ion  $m/e = 150$ . An alternative pathway is initiated by transfer of a hydrogen atom from a  $\text{CH}_2$  group to the ionized nitro group. Subsequent elimination of  $\text{N}(\text{C}_2\text{H}_5)(\text{C}_2\text{H}_4)$  produces the fragment  $\text{N}=\text{N-Phe-NOOH}$  ( $m/e = 151$ ), from which loss of  $\text{N}_2$  is feasible, and is indeed detected. Ionization at the nitrogen atom  $\text{N}^2$  results in a McLafferty rearrangement followed by the successive releases of  $\text{C}_2\text{H}_4$  and  $\text{N}_2$ . (This fragmentation pattern is analogous to route II in Fig. 4). The elemental composition of the fragments 151, 150, and 123 has been confirmed by high-resolution mass spectroscopy.

**Mass Spectroscopic Fragmentation Patterns of Pentazadienes and Hexazadiene.** A typical mass spectrum of pentazadiene compound **20** and the corresponding fragmentation reaction are shown in Fig. 4. From the  $\alpha$ -cleavage between the  $\text{N}^2$  and  $\text{N}^3$  nitrogen atoms, stable ions do result. Loss of nitrogen from the diazonium ion (route I in the scheme of Fig. 4) results in the substituted phenyl cation, which corresponds to the base peak of the spectrum. (In three additional spectra of **20**, it has been verified that the intensity ratio of masses 111 and 113 corresponds to the one expected from the relative abundance of the  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  isotopes.) The fragmentation pathway II, resulting from  $\alpha$ -cleavage between nitrogen atoms  $\text{N}^3$  and  $\text{N}^4$ , gives rise to ions detected in smaller concentrations. A McLafferty rearrangement, releasing  $\text{C}_2\text{H}_4$ , is followed by the loss of nitrogen. The corresponding fragments are also observed for compounds **17-19**.

We note that, in contrast to other investigations,<sup>22</sup> the molecular ion is detected in our pentazadiene mass spectra, although with very weak intensities. The fragment ions expected from the scheme of Fig. 4 have also been confirmed for 1,5-di(4-nitrophenyl)-3-*n*-butyl-pentaza-

TABLE VI. Relative intensities of prominent peaks in mass spectra of substituted triazenes.

Compound	$\text{M}^+$		Diazonium		Fragment subst. phenyl		Dialkyl-amino	
	$m/e$	Int. <sup>a</sup>	$m/e$	Int. <sup>a</sup>	$m/e$	Int.	$m/e$	Int.
<b>1</b>	220	86	148	25	120	100	72	4
<b>2</b>	177	31	105	40	77	100	72	6
<b>3</b>	207	51	135	50	107	100	72	4
<b>4</b>	191	23	119	20	91	100	72	5
<b>5</b>	221	39	149	30	121	100	72	17
<b>6</b>	202	20	130	19	102	100	72	3
<b>7</b>	222	37	150	44	122	100	72	7
<b>8</b>	315	71	243	91	215	100	72	9
<b>10<sup>b</sup></b>	193	46	149	56	121	100	44	12
<b>11</b>	221	27	149	24	121	100	72	14
<b>12</b>	249	25	149	22	121	100	100	21
<b>13</b>	249	27	149	18	121	100	100	30
<b>14</b>	222	36	150	57	122	100	72	9
<b>15</b>	222	44	150	100			72	15

<sup>a</sup> Intensities have been averaged over 10-30 spectra (cf. experimental section), and are given relative to the most intense peak, defined as 100.

<sup>b</sup> The mass spectrum of **9** could not be recorded as a consequence of insufficient volatility.

diene,<sup>23</sup> which was freshly synthesized and carefully purified prior to introduction into the mass spectrometer. The fact that a different fragmentation pattern has been reported for this compound in the literature<sup>23</sup> might be due to the difficulty of separating triazene and pentazadiene products by thin-layer chromatography, as had been used in Ref. 23.

For the pentazadiene **21** and the hexazadiene **16**, the main fragments from route I are observed. However, the molecular ion, as well as products from route II, is not detected.

## DISCUSSION

To test whether shifts in vibrational frequencies and changes in the relative intensities of the molecular ion can be traced to the same origin, we have plotted these quantities against each other in Fig. 5. Standard deviations are  $\leq 4\%$  for the relative ion intensities averaged from 30 mass spectra, and  $\leq 2 \text{ cm}^{-1}$  for the peak positions.

For the *para*-substituted compounds, excluding **2** and **4**, a satisfactory correlation is obtained ( $r = 0.93$ , solid line). With triazenes **2** and **4**, the additional possibility of primary ionization at a hetero-atom of the phenyl substituent does not exist; therefore, lower intensities of the molecular ion do result. Compound **2** shows a strong deviation from the correlation; i.e., the Raman frequency is higher than expected. As mentioned above, this observation is probably due to the significantly lower mass of the unsubstituted phenyl ring.

It has been proposed in the literature<sup>24,25</sup> that vibrational frequencies (C-H, N-H, O-H, S-H, C=N-, C=O, S=O,  $\text{NO}_2$ ) of substituents in aromatic compounds can be correlated with the Hammett parameter  $\sigma$ . To test this idea, we have plotted the  $\text{N}=\text{N}$  Raman stretching frequency of the *para*-substituted compounds **1** through **7** against the corresponding Hammett constants in Fig. 6. If all compounds are included, only a fair correlation is obtained ( $r = -0.90$ ); upon omission of triazene **2** (no

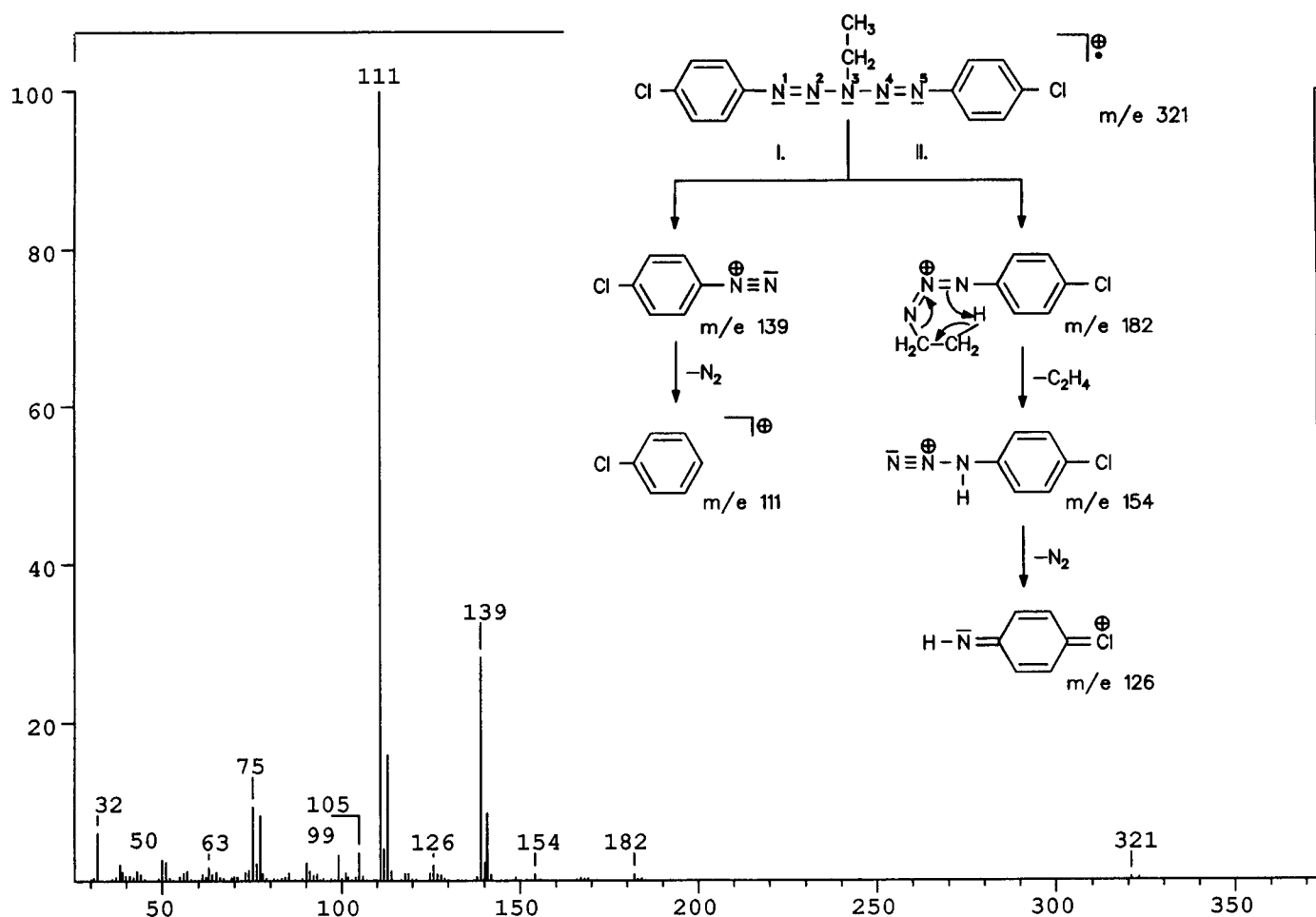


FIG. 4. Mass spectrum of 1,5-di(4-chlorophenyl)-3-ethyl-pentazadiene (compound 20). The suggested fragmentation scheme is shown as an inset.

substituent at the phenyl ring), the correlation becomes satisfactory ( $r = -0.97$ ).

The series of compounds where the alkyl-substituents are varied (10-13) shows the following trends. With increasing inductive effect of the alkyl groups (Me < Et < Prop), the Raman shift increases while the intensity of the molecular ion decreases. For compounds 11, 12, and 13 only minor changes are found in the Raman as well as in the mass spectra. It is only compound 10 that

deviates significantly from the other members of the series, both with respect to  $\tilde{\nu}(\text{N}=\text{N})$  and to the relative fragment intensities.

## CONCLUSIONS

From the mass spectroscopic intensity data presented for 1-phenyl-3,3-dialkyl-triazenes, we conclude that the molecular ion is stabilized by electron-donating substituents on the phenyl ring. In contrast, electron-with-

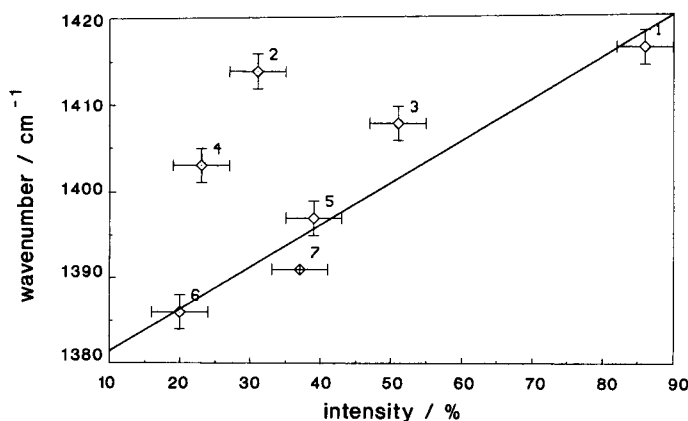


FIG. 5. Correlation of N=N stretching frequency with the relative parent ion intensity, as derived from the mass spectrum, for *para*-substituted 1-phenyl-3,3-dialkyl-triazenes.

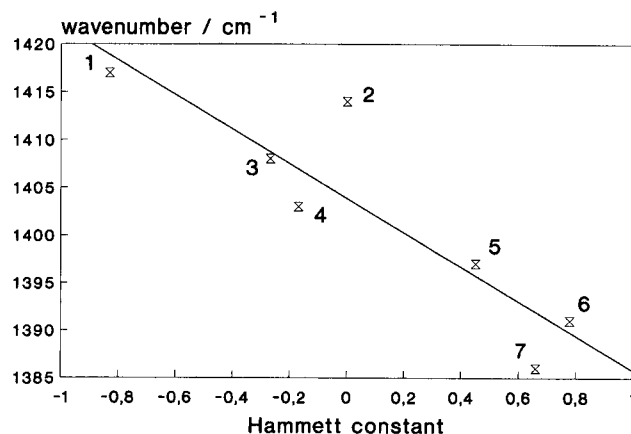


FIG. 6. Correlation of N=N stretching frequency with the Hammett constant  $\sigma$  for *para*-substituted 1-phenyl-3,3-dialkyl-triazenes.

drawing groups promote the development of a 1,3-dipolar structure, and thereby decrease the strength of the formal double bond in the triazeno group. Both trends have been confirmed for the *para*-substituted compounds from the observed Raman frequencies of the N=N stretching modes. Compounds with electron-donating groups are characterized by the highest Raman shifts, and by molecular ions with the greatest intensity.

Bulky N<sup>3</sup>-alkyl substituents tend to slow down the internal rotation; the associated electron-donating effect decreases the N<sup>1</sup>=N<sup>2</sup> bond order and the associated Raman frequency. Simultaneously, the stability of the molecular ions is decreased, as the +I inductive effect of the -C<sub>2</sub>H<sub>5</sub> and -C<sub>3</sub>H<sub>7</sub> groups promotes the N<sup>2</sup>-N<sup>3</sup> bond breakage. In agreement with this statement, compound **10** carrying the less heavy -N(CH<sub>3</sub>)<sub>2</sub> end group exhibits a high N=N bond order and a stable molecular ion. [The low vibrational frequencies (both  $\nu_s$  and  $\nu_{as}$ ) deviate from the trends observed with the other compounds.]

Pentazadiene and hexazadiene compounds exhibit a smaller tendency for a 1,3-dipolar charge delocalization, and therefore show more or less constant Raman frequencies, as well as intensities of the molecular ion. Compound **21** represents an exception; for this triphenylpentazadiene, the bond from the central nitrogen atom to the attached phenyl ring has partial double bond character. As a consequence of the increased delocalization, the N=N vibration is shifted to lower wavenumbers.

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