^{13}C AND ^{15}N NMR SPECTRA OF 1-(3- OR 4-SUBSTITUTED PHENYL)-3-METHYL-3-PHENYLTRIAZENES

Antonín LYČKA[a] and Pavel VETEŠNÍK[b]

[a] *Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví and*
[b] *Department of Organic Chemistry,*
Institute of Chemical Technology, 532 10 Pardubice

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^{13}C and ^{15}N NMR spectra of ten 1-(3- or 4-substituted phenyl)-3-methyl-3-phenyltriazenes have been measured in deuteriochloroform. In the temperature range from 210 to 320 K the ^{13}C NMR signals of both methyl and phenyl groups were not broadened, and no free rotation of the substituents at $N_{(3)}$ has been proved. From the values $^2J(^{15}N_{(2)}\,^{13}C_{(5')})$ and $^2J(^{15}N_{(2)}\,^{13}C_{(1')})$ it was possible to determine conformation at the $N_{(2)}$—$N_{(3)}$ bond which has partial double bond character. The value $^1J(^{15}N_{(1)}\,^{13}C_{(1)})$ is equal to 1·0 Hz, which proves *trans* arrangement of the substituents at the $N_{(1)}$=$N_{(2)}$ bond.

Triazenes have both cancerogenic and cancerostatic properties[1]; they contain extensive π system enabling charge delocalization, and they often were studied by means of ^1H, ^{13}C, ^{15}N and ^{19}F NMR spectroscopy (refs[1-11] and the literature cited therein). The disubstituted triazenes were investigated with respect to tautomerism[3-7,10,12-16] and the trisubstituted compounds were mainly studied from the point of view of hindered rotation at the $N_{(2)}$—$N_{(3)}$ bond[1,2,11,17].

The aim of the present work was to measure the ^{13}C and ^{15}N chemical shifts in 1-(3- or 4-substituted phenyl)-3-methyl-4-phenyltriazenes *I* and to study the substituent and temperature effects on these chemical shifts.

EXPERIMENTAL

The 1-(3- or 4-substituted phenyl)-3-methyl-3-phenyltriazenes *Ia*—*Ij* were prepared by coupling of the respective diazonium salts with N-methylaniline[18]. The ^{15}N-labelled trizenes were prepared with the use of ^{15}N-labelled chemicals: $Na^{15}NO_2$ (95% ^{15}N), aniline (95% ^{15}N), 4-bromoaniline (95% ^{15}N), and 4-nitroaniline (10% ^{15}N) (Isocommerz, Berlin). $(^{15}N)_3$-Diphenylmethyltriazene was prepared by alkylation of $(^{15}N)_3$-diphenyltriazene with methyl iodide[19].

The ^{13}C and ^{15}N NMR spectra were measured at 25·047 and 10·095 MHz, respectively, using a JNM-FX 100 (JEOL) apparatus equipped with multinuclear tunable probe and quadrature detection and operating in FT mode. The mesaurements were carried out in 10 mm (o.d.) NMR test tubes within the range 210—320 K. For the measurements of ^{13}C NMR spectra we used 20—30% (w/v) solutions of the compounds in deuteriochloroform which served as an internal

lock substance. The following parameters were used for obtaining the ^{13}C chemical shifts: 5000 Hz spectral width, 8 K, 9 μs (35°) pulse width, pulse repetition 3 s, the proton noise decoupling. The carbon chemical shifts were related to tetramethylsilane as internal standard. The coupling constants $^{n}J(^{15}N^{13}C)$ were measured in 2–4% (w/v) solutions of the ^{15}N-labelled compounds at a digital resolution of 0·24 Hz/point and with the proton noise decoupling. After measuring the ^{13}C NMR spectra, we added chromium(III) acetylacetonate (25 mg $Cr(acac)_3$/ml) to the 20–30% solutions of the compounds and measured the ^{15}N NMR spectra at the ^{15}N natural abundance level. The following parameters were used: 4 000 Hz spectral width, 8 K, 15 μs (45°) pulse width, pulse repetition 5 s, the proton noise decoupling, accumulation time 6–14 h. The ^{15}N chemical shifts in the ^{15}N-labelled compounds were measured in 2–4% solutions with the use of the following parameters: 5 000 Hz spectral width, 8 K, 10 μs pulse width, pulse repetition 15 s, inverse-gated decoupling (irradiation during the acquisition time). The coupling constants $^{n}J(^{15}N^{15}N)$ were measured at a digital resolution of 0·24 Hz/point. All the ^{15}N chemical shifts are related to external neat nitromethane (25% ^{15}N) (ref.[20]).

RESULTS AND DISCUSSION

The ^{13}C chemical shifts in 1-(3- or 4-substituted phenyl)-3-methyl-3-phenyltriazenes *Ia–Ij* were assigned on the basis of the proton-coupled spectra, using the values of substituent chemical shifts[21] (SCS) and mutual comparison of the individual derivatives. The values of ^{13}C chemical shifts are given in Table I. For the ^{15}N-labelled derivatives we measured the absolute values of $^{n}J(^{15}N^{13}C)$ coupling constants (Table II). The ^{15}N chemical shifts were assigned on the basis of ^{15}N selective labeling and comparison with the published values[7–11]. The values $\delta(N_{(1)})$ and $\delta(N_{(3)})$ are very close (α effect[22]) to the corresponding values of diphenyltriazene (−9 and −300 ppm)[10] in acetone at −90°C when the proton only is at one of the $N_{(1)}$, $N_{(3)}$ nitrogen atoms. The signal of $N_{(1)}$ in compound *Ij* was differentiated from that of the nitro group by comparison with the chemical shifts of the triazene prepared with the use of $O_2NC_6H_4\ ^{15}NH_2$, and the assignment of analogous signals of compound *Ii* follows from the analogy with the $\delta(NO_2)$ values of substituted nitrobenzenes[23]. Table III gives the values of ^{15}N chemical shifts of the compounds *Ia–Ij*. All $^{n}J(^{15}N^{15}N)$ coupling constants were determined in $(^{15}N)_3$-diphenylmethyltriazene: $^{1}J(N_{(1)}N_{(2)}) = 12{\cdot}7$ Hz, $^{1}J(N_{(2)}N_{(3)}) = 14{\cdot}2$ Hz, and $^{2}J(N_{(1)}N_{(3)}) = 5{\cdot}9$ Hz (±0·3 Hz). Further $^{1}J(^{15}N^{15}N)$ values were measured in the ^{15}N doubly labelled compounds *Ie* and *Ij*: $^{1}J(N_{(1)}N_{(2)})$ is 12·5 and 12·9 Hz, respectively. The ^{15}N isotopic chemical shifts were observed in the ^{15}N doubly labelled compounds *Ie* (95% $^{15}N_{(1)}$; 10% $^{15}N_{(2)}$) and *Ij* (10% $^{15}N_{(1)}$; 95% $^{15}N_{(2)}$). The signals for $N_{(1)}$ (*Ie*) and $N_{(2)}$ (*Ij*), respectively, show upfield shifts by 1·7 Hz (0·17 ppm) and 1·0 Hz (0·1 ppm) when comparing the $^{15}N{=}^{15}N$ system with $^{15}N{=}^{14}N$ (*Ie*) and $^{14}N{=}^{15}N$ (*Ij*), respectively. Similar values were measured[24] for N=N group in azo dyestuffs containing amino or acetylamino group. The ^{19}F chemical shifts −37·5 and 16·7 ppm were measured for the compounds *Id* and *Ig*, respectively (related to external neat CF_3COOH).

The ^{13}C chemical shifts of the compounds *Ia*, *Ib*, *Ie*, and *Ij* (selected according to σ values) were measured in the range 210–320 K by steps of about 20°. Values of these chemical shifts are given in Table I. No broadening of the ^{13}C signals of methyl and phenyl groups was observed in the whole temperature range mentioned, which can be explained in two ways: (*i*) there exists free rotation around the $N_{(2)}$—$N_{(3)}$ bond (the coalescence temperature for a possible hindered rotation being below 210 K) or, on the contrary, (*ii*) there exists hindered rotation around the $N_{(2)}$—$N_{(3)}$ bond, the coalescence temperature being above 320 K, and, hence, only one of the conformers is present. This problem was solved by measuring temperature dependence of absolute values of the coupling constants $^2J(^{15}N_{(2)}{}^{13}C_{(1')})$ and $^2J(^{15}N_{(2)}\cdot\cdot{}^{13}C_{(5')})$. It is known that the $^2J(^{15}N^{13}C)$ values are stereospecific, which can, *e.g.*, be documented[25] in the case of compounds *II* whose $^2J(NCN) = 1-2{\cdot}2$ Hz and $^2J(NCOO) \sim 10{\cdot}5$ Hz. Table II gives the values $^2J(^{15}NN^{13}C_{(1')})$ and $^2J(^{15}NNC_{(5')})$

TABLE I

The ^{13}C chemical shifts (δ scale; $\pm 0{\cdot}05$ ppm) in compounds *Ia*–*Ij* in deuteriochloroform at 300 K

Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(4')}$	$C_{(5')}$
Ia	150·2	121·2	128·8[a]	126·5	128·8[a]	121·2	145·0	116·8	128·9[a]	123·1	32·0
Ia[b]	150·4	121·3	128·8[a]	126·5	128·8[a]	121·3	145·4	116·9	128·9[a]	123·3	32·0
Ia[c]	149·7	121·0	128·8	126·4	128·8	120·9	144·4	116·4	128·8	123·1	32·1
Ib[d]	144·1	122·3	114·1	158·5	114·1	122·3	145·3	116·6	129·0	123·0	31·9
Ib[c,e]	143·4	122·0	113·7	157·7	113·7	122·0	144·7	116·3	129·0	122·9	32·2
Ic[f]	148·0	121·1	129·5	136·3	129·5	121·1	145·2	116·7	129·0	123·1	32·0
Id[g]	146·5	122·5	115·6	161·4	115·6	1225·	145·0	116·9	129·1	123·4	32·2
Ie	149·3	122·8	131·9	119·8	131·9	122·8	144·9	117·2	129·1	123·8	32·5
Ie[b]	149·5	122·9	132·0	119·9	131·0	122·9	145·1	117·3	129·2	123·8	32·5
Ie[c]	148·6	122·5	131·8	119·5	131·8	122·5	144·5	116·8	129·0	123·6	32·8
If	151·5	123·6[a]	122·7	129·0	130·1	120·5	144·7	117·2	129·0	123·8[a]	32·6
Ig[h]	153·0	121·4	126·0	127·9	126·0	121·4	144·8	117·4	129·2	124·2	32·8
Ih[i]	154·1	121·3	128·2	137·1	128·2	121·3	144·2	117·3	129·0	124·4	33·0
Ii	151·2	115·6	148·7	120·4	129·4	127·1	144·3	117·4	129·1	124·3	32·9
Ij	155·1	121·4	124·8	145·5	124·8	121·4	144·4	117·8	129·3	124·9	33·5
Ij[b]	155·3	121·5	124·8	145·7	124·8	121·5	144·6	117·9	129·3	125·0	33·4
Ij[c]	154·8	121·2	124·9	144·6	124·9	121·2	143·9	117·5	129·1	124·9	33·8

[a] The assignment can be opposite; [b] 320 K; [c] 210 K; [d] $\delta(OCH_3) = 55{\cdot}4$; [e] $\delta(OCH_3) = 55{\cdot}3$; [f] $\delta(CH_3) = 21{\cdot}0$; [g] $|^nJ(^{19}F^{13}C)| = 245{\cdot}3$ ($n = 1$); 22·5 ($n = 2$); 8·1 ($n = 3$); 3·2 ($n = 4$) Hz; [h] $\delta(CF_3) = 124{\cdot}3$; $|^nJ(^{19}F^{13}C)| = 271{\cdot}9$ ($n = 1$); 33·0 ($n = 2$); 3·8 ($n = 3$) Hz; [i] $\delta(SO_2CH_3) = 44{\cdot}4$.

TABLE II

Absolute values of the coupling constants $^{n}J(^{15}N^{13}C)$ (Hz, ±0·3 Hz) in compounds *Ia*, *Ie*, and *Ij* in deuteriochloroform

Compound 95%	^{15}N	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(5')}$	$C_{(4')}$
Ia[a]	$N_{(2)}$	7·9	3·9	[b]	[b]	6·5	2·6	[b]	[b]	1·8
Ie[a]	$N_{(1)}$	1·0	4·1	2·0	0·7	1·1	0·4	[b]	[b]	3·7
Ij[a]	$N_{(2)}$	8·0	4·1	[b]	[b]	6·5	2·6	[b]	[b]	2·0
Ij[c]	$N_{(2)}$	8·1	4·0	[b]	[b]	6·3	2·6	[b]	[b]	1·8
Ij[d]	$N_{(2)}$	8·0	4·1	[b]	[b]	6·5	2·5	[b]	[b]	1·8

[a] 300 K; [b] <0·7 Hz; [c] 330 K; [d] 240 K.

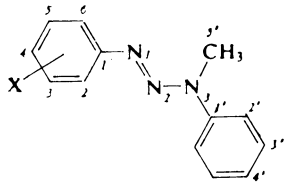
TABLE III

The ^{15}N chemical shifts (±0·2 ppm) in the compounds *Ia*–*Ij* in deuteriochloroform and σ values of the substituents

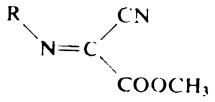
Compound	$\delta(^{15}N_{(1)})$	$\delta(^{15}N_{(2)})$	$\delta(^{15}N_{(3)})$	σ^-
Ia[a]	−5·2	61·5	−205·8	0·00
Ia[b]	−6·7	60·2	−207·4	0·00
Ia[c]	−5·7	62·4	−205·4	0·00
Ib[b]	−6·2	55·6	−210·0	−0·12
Ic[b]	−6·0	58·6	−208·7	−0·14
Id[b]	−9·3	59·7	−207·5	0·15
Ie[b]	−11·0	61·2	−205·6	0·26
Ie[c]	−9·7	62·6	—	—
If[b]	−11·5	62·5	−204·2	0·37
Ig[b]	−13·0	64·3	−203·4	0·62
Ih[b]	−15·4	66·5	−199·5	1·05
Ii[b,d]	−16·2	64·5	−201·5	0·71
Ij[b,e]	−16·5	67·8	−198·4	1·25
Ij[b,f]	−17·1	67·9	—	—
Ij[g]	—	68·7	—	—

[a] 60% solution; [b] about 25% solution with addition of 25 mg $Cr(acac)_3$ per 1 ml; [c] the ^{15}N doubly labelled compound; [d] $\delta(NO_2) = -10·8$; [e] $\delta(NO_2) = -11·2$; [f] the ^{15}N doubly labelled compound with addition of 25 mg $Cr(acac)_3$ per 1 ml; [g] the ^{15}N-labelled compound.

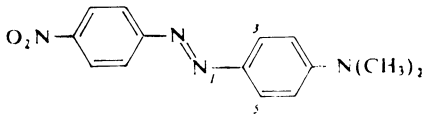
measured at 230, 300, and 330 K for the compound *Ij*. Obviously these constants are temperature independent within experimental error. For the azo dyestuff *III* it was



I



II



III

found[26] that the coupling constant $^2J(^{15}N_{(1)}{}^{13}C)$ was temperature dependent, at 265 K the values being $^2J(^{15}N_{(1)}{}^{13}C_{(3)}) < 1{\cdot}5$ Hz and $^2J(^{15}N_{(1)}{}^{13}C_{(5)}) = 10$ Hz, whereas at free rotation (303 K) a single value of the ^{13}C chemical shift for $C_{(3)}$ and $C_{(5)}$ and a single value of the coupling constant $^2J(^{15}N_{(1)}{}^{13}C_{(3',5')}) = 4{\cdot}7$ Hz were found. From the given facts it follows that in the case of compounds *Ia*–*Ij* there exists hindered rotation with high $\Delta G^{\neq}$ values, hence the $N_{(2)}$—$N_{(3)}$ bond has partial double-bond character. From the $^2J(^{15}N_{(2)}{}^{13}C_{(1)})$ values (Table II) of compounds *Ia* and *Ij* then follows that the substituents at the $N_{(1)}{=}N_{(2)}$ bond have *trans* arrangement, because these values are very similar to the values of $^2J(^{15}N_{(2)}\cdot{}^{13}C_{(1')})$, and, hence, the substituent must be in the same geometrical position with respect to free electron pair at the $N_{(2)}$ nitrogen atom. Recently it was found[27] that also the $^1J(^{15}N^{13}C)$ values depend on configuration at the double bond: for *cis*

TABLE IV

Values of the correlation parameters of Eq. (*1*), N = 10

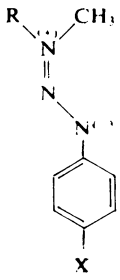
(X)	*a*	*b*	*r*	*F*-test
$\delta(N_{(1)})$	−8·07 ± 0·91	−7·08 ± 0·56	0·9532	79·5
$\delta(N_{(2)})$	7·49 ± 0·77	59·0 ± 0·47	0·9607	95·9
$\delta(N_{(3)})$	8·05 ± 0·47	−207·9 ± 0·29	0·9866	292·3
$\delta(C_{(4')})$	1·36 ± 0·11	123·2 ± 0·07	0·9764	163·2
$\delta(C_{(5')})$	1·05 ± 0·07	32·12 ± 0·04	0·9827	225·6

and *trans* 4-methylazobenzene the respective values are 9·3 and 1·2 Hz. Also for substituted triazenes[27] the coupling constants are different: 7·7 and 0 Hz for *cis* and *trans* arrangement at the N=N bond, respectively. For compound *Ie* the found coupling constant $^1J(^{15}N_{(1)}{}^{13}C_{(1)}) = 1{\cdot}0$ Hz (Table II) corresponds to the *trans* derivative, and this fact agrees with the above-given results following from the values $^2J(^{15}N_{(2)}{}^{13}C)$ of compounds *Ia* and *Ij*.

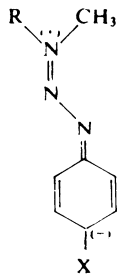
The values of chemical shifts of $N_{(1-3)}$ nitrogen atoms and $C_{(1')}$ and $C_{(5')}$ carbon atoms correlate better with σ^- than with σ constants. The values of σ^- were taken from ref.[28], and the values σ_m were used for the 3-substituted derivatives. The parameters of the correlation equation (*1*)

$$\delta(X) = a\sigma^- + b \qquad (1)$$

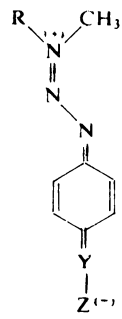
are given in Table IV. Values of the correlation coefficients are lower than it is usual for, *e.g.*, kinetic data, but it must be taken into account that difference in the ^{13}C chemical shifts is relatively small as compared with experimental error, and in the case of the ^{15}N chemical shifts the addition of $Cr(acac)_3$ can affect slightly the ^{15}N chemical shifts of some compounds, because it can act as a shift reagent[23]. Both the hindered rotation around the $N_{(2)}$—$N_{(3)}$ bond and the therewith connected correlation of the chemical shifts with the σ^- constants correspond to contribution of polar structures.



A



B



C

The structures *A* and *B* given in ref[8] for R = CH_3 can be complemented by structure *C* for some derivatives *I* (*e.g.*, 4-NO_2 and 4-SO_2CH_3) in which the negative charge is localized at at the substituent. Similar results were obtained in the study of tautomerism of alkylaryltriazenes[6] as well as in a study of rotation of trialkyltriazenes and aryldialkyltriazenes[1].

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ERRATA

^{13}C AND ^{15}N NMR SPECTRA OF 1-(3- OR 4-SUBSTITUTED PHENYL)-3-METHYL--3-PHENYLTRIAZENES

Antonín Lyčka and Pavel Vetešník

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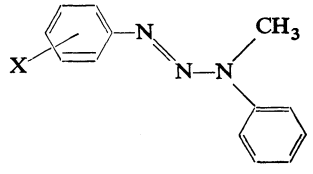
In this paper the following correction should be made (p. 967):



I

Ia, X = H
Ib, X = 4-OCH_3
Ic, X = 4-CH_3
Id, X = 4-F
Ie, X = 4-Br
If, X = 3-Br
Ig, X = 4-CF_3
Ih, X = 4-SO_2CH_3
Ii, X = 3-NO_2
Ij, X = 4-NO_2