Asymmetric Nitrogen. Part 75.[1] Stereochemistry of Diaziridinyl Radicals

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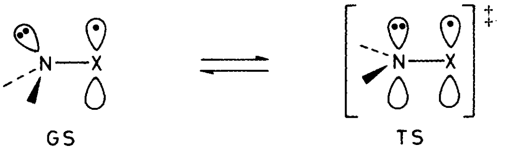
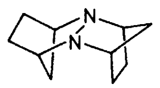
ESR spectra have been recorded for the 3,3-dimethyl-, 3,3-bis(trifluoromethyl)- and 3,3-bis(methoxycarbonyl)-2-alkyldiaziridinyls (**6**)–(**10**), as well as the bicyclic diaziridinyls (**13**)–(**15**), generated by the photolysis of 5-substituted *exo*-6-chloro-1,6-diazabicyclo[3.1.0]hexanes. Theoretical *ab initio* MO calculations (UHF 3-21G) on the simplest diaziridinyl (**5**) have been performed. Diaziridinyl radicals in the ground state have a pyramidal configuration at the trico-ordinated nitrogen atom. The difference between the theoretically calculated inversion barriers of diaziridinyl (**5**) and diaziridine (**11**) is 67.2 kJ mol^{-1} and between the experimental inversion barriers of 2-isopropyl-3,3-bis(trifluoromethyl)diaziridinyl (**7**) and the corresponding NH-diaziridine is 78.7 kJ mol^{-1}. The bicyclic diaziridinyls (**13**)–(**15**) prefer the boat conformation.

The nitrogen inversion barrier in the $R^1_2\ddot{N}$–$\dot{X}$: radical or $R^1_2\ddot{N}$–$\overset{+\bullet}{X}$–R^2 radical cation must be substantially lower than in the parent compound $R^1_2\ddot{N}$–$\ddot{X}$–R^2 because of the stronger interaction of the semioccupied p orbital with the n_N orbital with pure p character in the planar transition state (TS) (Scheme 1).



Scheme 1.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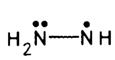
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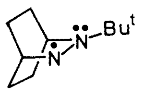
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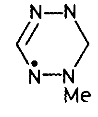
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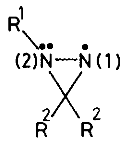

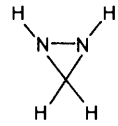
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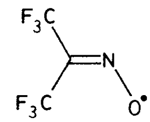

(12)

(5) $R^1 = R^2 = H$
(6) $R^1 = R^2 = Me$
(7) $R^1 = Pr^i, R^2 = CF_3$
(8) $R^1 = CH_2CO_2Et, R^2 = CF_3$
(9) $R^1 = CH(Me)CO_2Et, R^2 = CF_3$
(10) $R^1 = Me, R^2 = CO_2Me$

This is confirmed, in particular, by the comparison of double nitrogen inversion barriers for sesquibicyclic hydrazine (**1**) (113.0 kJ mol^{-1}) and its radical cation (19.5 kJ mol^{-1}).[2]

For neutral hydrazyl radicals there are not experimental data on the pyramidal stability of trico-ordinated nitrogen. Moreover, the question of the stereochemical configuration of this atom in the ground state (GS) of hydrazyls which do not contain π-acceptor ligands is debatable. Thus, according to *ab initio* (STO 3G)[3] and INDO[4] quantum chemical calculations for the simplest hydrazyl (**2**), the N(2) atom has a pyramidal configuration with an inversion barrier of 25.1 kJ mol^{-1} (*ab initio*[3]). However, the calculation for hydrazyl (**2**) in the extended 4-31G basis set yields a planar configuration at the N(2) atom.[3] The same configuration is assumed for the N(3) atom in the bicyclic hydrazyl (**3**), based on the ESR data,[5] whereas in the case of verdazyl (**4**) the temperature dependence of the hyperfine coupling constant on N(1) and N(5) nuclei is explained by pyramidal inversion.[6] An investigation of hydrazyls with the maximum possible pyramidal stability of trico-ordinated nitrogen will obviously make it possible to clear up the situation to a considerable extent. Such hydrazyls seem to be represented by diaziridinyl radicals, since the initial diaziridines have the highest nitrogen inversion barrier (92–113 kJ mol^{-1})[7,8] in the series of NH-hydrazines. For this reason a theoretical and experimental study of the stereochemistry of diaziridinyls (**5**)–(**10**) has been undertaken in the present work.

Results and Discussion

According to our theoretical *ab initio* MO calculation on the simplest diaziridinyl (**5**), the pyramidal configuration of the trico-ordinated N(2) atom corresponds to the energy minimum. The calculated difference between the energies of the GS and TS of the radical (**5**) is considerably smaller than in the case of the corresponding diaziridine (**11**) (Table 1). It can be assumed that the low nitrogen inversion barrier of the diaziridinyl (**5**) is caused not only by three-electron $n_{N(1)}$–$p_{N(2)}$ stabilization of the TS but also by four-electron $n_{N(1)}$–$n_{N(2)}$ destabilization of the GS. Indeed, in contrast to TS-(**5**), in GS-(**5**) the n_N orbitals are not orthogonal (Scheme 2). On the contrary, in the case of diaziridine (**11**) the torsion angles between the axes of the n_N orbitals are such that the TS is destabilized to a greater extent. An increase in three-electron interaction in going from GS-(**5**) to TS-(**5**) follows from the delocalization of spin density between the N(1) and N(2) atoms, as well as from the shortening of the N–N bond (Table 1) [which is greater than expected, owing to the N(2) atom rehybridization].

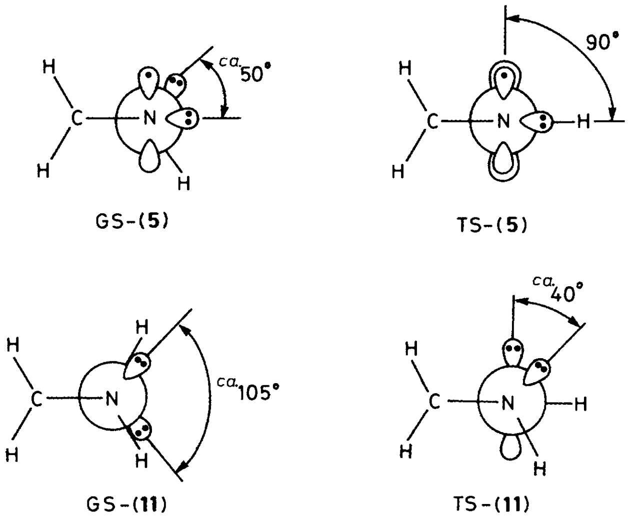
Experimental studies on the stereochemistry of diaziridinyls have been performed using the ESR technique on radicals (**6**)–(**9**), generated by the photolysis of the corresponding NH-diaziridines in $(Bu^tO)_2$. Diaziridinyls of type (**10**), previously described by Forrester and Sadd,[9] are unsuitable for solving this problem because they contain no indicator groups at C(3).

The ESR spectra of diaziridinyls (**6**)–(**9**) (Table 2, Figure 1) correspond to hyperfine splitting only with one CH_3 or CF_3

Table 1. Some calculated (3-21G) geometric, electronic and energetic parameters for the ground and transition-state structures for the nitrogen inversion of diaziridinyl (**5**) and the corresponding diaziridine (**11**).[8]

	Diaziridinyl (UHF) GS	Diaziridinyl (UHF) TS	Diaziridine (RHF) GS[a]	Diaziridine (RHF) TS[b]
Bond length/Å				
N(1)–N(2)	1.503	1.400	1.530	1.475
C(3)–N(1)	1.507	1.572	1.475	1.540
C(3)–N(2)	1.460	1.403	1.475	1.391
N(2)–H	1.010	0.986	1.010	0.984
Sum of valence angles at N(2)/°	286.1	360	275.5	359.4
Spin density				
N(1)	1.3275	1.2852		
N(2)	−0.0540	0.3103		
C(3)	−0.1736	−0.2236		
$H_{N(2)}$	0.0271	−0.0153		
Relative energy/kJ mol^{-1}	0[c]	46.2	0[d]	113.4

[a] 1,2-*trans*-Diaziridine. [b] Monoplanar transition state.[8] [c] Total energy $E_T = -147.5423$ hartree. [d] $E_T = -148.1464$ hartree.



Scheme 2.

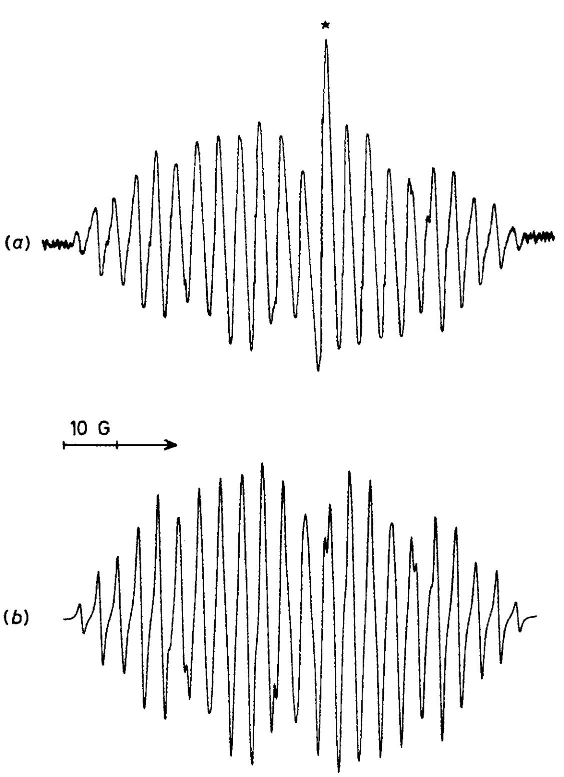


Figure 1. (*a*) ESR spectrum of diaziridinyl (**8**) at 253 K; The asterisk indicates a 'quartz signal.' (*b*) Computer simulation of (*a*); hyperfine coupling constants are as given in Table 2, linewidth is 0.7 G, lineshape is Lorentzian.

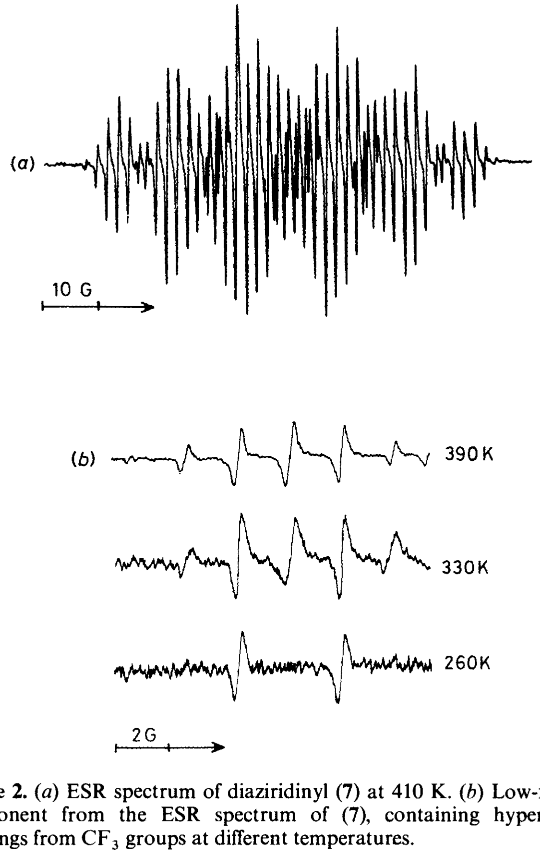


Figure 2. (*a*) ESR spectrum of diaziridinyl (**7**) at 410 K. (*b*) Low-field component from the ESR spectrum of (**7**), containing hyperfine splittings from CF_3 groups at different temperatures.

group at C(3), which confirms the N(2) atom pyramidal stability, on the ESR time scale. In the case of diaziridinyl (**7**), the quartet at 293 K, owing to hyperfine splitting with one CF_3 group, is transformed into a septet (1:6:15:20:15:6:1) at 390 K, caused by hyperfine splitting with two equivalent CF_3 groups. This transformation in the intermediate temperature range has a clear-cut pattern of linewidth alternation (Figure 2) and indicates unambiguously the presence of intramolecular dynamic effects caused by the inversion process. From an analysis[10] of the temperature-dependence of the lineshape in the ESR spectra of diaziridinyl (**7**), the rate constants for N(2) atom inversion were determined (Table 3). The difference in nitrogen inversion barriers between radical (**7**) and the corresponding NH-diaziridine[7] ($\Delta\Delta G^{\ddagger}_{inv} = 78.7$ kJ mol^{-1}) is comparable to that theoretically calculated for the diaziridinyl (**5**)/diaziridine (**11**) pair (67.2 kJ mol^{-1}). A certain decrease in the nitrogen pyramidal stability in CF_3-substituted diaziridinyl (**7**), as in the case of 3,3-bis(trifluoromethyl)diaziridines,[8,11] seems to be

Table 2. Parameters for the ESR spectra of diaziridinyls (**6**)–(**10**) and (**13**)–(**15**).

Compound	T/K	Hyperfine coupling constants/G			g-Factor
		^{a}N(1)	^{a}N(2)	a(others)	
(**6**)	293	11.5	15.5	2.0 (3 H, MeC) 2.0 (3 H, MeN)	2.0041
(**7**)	293	11.25	16.7	9.25 (1 H) 4.0 (3 F)	2.0034
	400	11.25	16.7	9.25 (1 H) 2.0 (6 F)	
(**8**)	253	11.5	16.0	7.5 (2 H) 3.5 (3 F)	2.032
(**9**)	293	11.5	18.0	8.5 (1 H) 3.15 (3 F)	2.0035
(**10**)	293	11.0	18.0	2.6 (3 H)	2.0035
^{15}N(1)–(**10**)	293	15.5	18.0	2.6 (3 H)	
(**13**)	193	12.0[a]	16.5[b]	3.5 (1 H) 1.75 (3 H)	2.0038
(**14**)	213	12.0[a]	15.5[b]	3.5 (1 H) 1.75 (3 H)	2.0038
(**15**)	223	12.0[a]	15.5[b]	3.5 (1 H) 1.75 (3 H)	2.0038

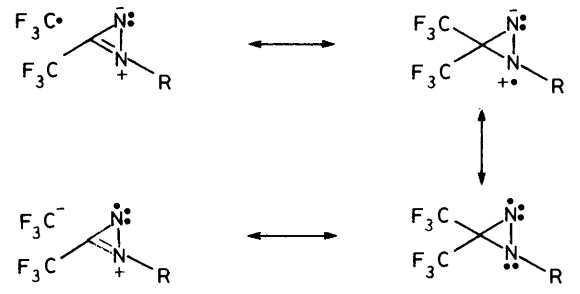
[a] Hyperfine splitting on the nucleus of the bico-ordinated N(6) atom. [b] Hyperfine splitting on the nucleus of the trico-ordinated bridgehead nitrogen atom.

Table 3. First-order rate constants and kinetic parameters[a] for inversion of diaziridinyl (**7**)[b] in $(Bu^tO)_2$.

T/K	$k/10^8$ s^{-1}	$\Delta G^{\ddagger c}$/kJ mol^{-1}	E_a/kJ mol^{-1}	$\Delta H^{\ddagger}_{298}$/kJ mol^{-1}	log (A/s^{-1})	$\Delta S^{\ddagger}_{298}$/J mol^{-1} K^{-1}
260	0.5	25.1	18.3 ± 3.1	15.9 ± 3.1	11.4 ± 0.5	35.8 ± 9.6
298	1.3	26.7				
300	1.3	26.9				
330	3.4	27.2				
370	5.0	29.7				
400	10.0	30.0				

[a] Kinetic parameters were obtained from the slope and intercept on the ordinate of the best-straight line (linear least-square) plot of ln k *vs.* T^{-1}; error is for 95% confidence limits. [b] The nitrogen inversion barrier for the corresponding 1-isopropyl-3,3-bis(trifluoromethyl)diaziridine[7] is 105.4 kJ mol^{-1} at 298 K. [c] $\Delta G^{\ddagger}$ values were obtained from the Eyring equation.

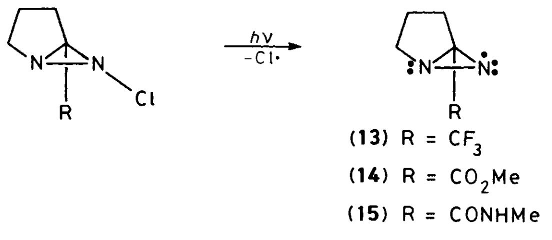
caused by additional TS stabilization resulting from an n_N-$\pi^*_{C(CF_3)_2}$ interaction (Scheme 3).



Scheme 3.

We had no success in measuring the nitrogen inversion barriers for diaziridinyls (**6**), (**8**) and (**9**). The ESR spectrum of radical (**6**) does not change on heating to 400 K, and when diaziridinyls (**8**) and (**9**) are heated, a secondary radical is observed which by ESR spectroscopy ($a_N = 31.2$ G, a_F^1 *ca.* 7.0 G, $a_F^2 \leqslant 1$ G) corresponds to the iminoxyl radical (**12**).[12] A similar transformation into iminoxyls was observed earlier[9] for diaziridinyls of type (**10**).

The values of both nitrogen hyperfine coupling constants for diaziridinyl (**10**) are close to those measured for radicals (**6**)–(**9**), and, therefore, the pyramidal configuration at trico-ordinated nitrogen can be assumed in *N*-alkyl substituted 3,3-bis(alkoxycarbonyl)diaziridinyls.[9] Similar a_N values were also obtained for bicyclic diaziridinyls (**13**)–(**15**) (Table 2), where the trico-ordinated nitrogen atom is known to be pyramidal, since it is located at the bridgehead of the bicyclic system. These diaziridinyls, as distinct from the others, were generated directly by the photolysis of the corresponding *N*-chlorodiaziridines in a toluene–pentane (1:2) mixture or, in the case of (**15**), in tetrahydrofuran (Scheme 4).



Scheme 4.

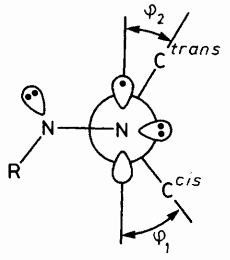
Bicyclic diaziridinyls (**13**)–(**15**) can be observed at relatively low temperatures (Table 2). The low stability of these radicals, by comparison with monocyclic diaziridinyls (**6**)–(**10**), can be explained by the steric weakening of the stabilizing three-electron n_N-p_N interaction. It is also necessary to note that only diaziridinyl (**7**) is revealed in the ESR spectra several seconds after the irradiation has stopped.

A change in the nature of the substituent at trico-ordinated nitrogen in diaziridinyls has a greater effect on the higher value hyperfine coupling constants (a_N) than those with lower values

(Table 2). Therefore, in contrast to the assignment made by Forrester and Sadd[9] the larger nitrogen hyperfine coupling constant can be assigned to $a_{N(2)}$ and the smaller one to $a_{N(1)}$. This was unambiguously confirmed by insertion of ^{15}N label at position 1 in diaziridinyl (**10**). In this case the smaller a_N constant increased and the larger one did not change (Table 2).

A three-electron n_N–p interaction, with formation of an α-radical centre, leads to flattening of the trico-ordinated nitrogen pyramid. In the case of diaziridinyl (**5**) the sum of the valence angles at the N(2) atom is greater by 10.6° than in the corresponding diaziridine (**11**) (Table 1). Therefore, in accordance with the concept of an increase in a_N with increasing s-character of the n_N orbital,[13] one would expect a greater hyperfine coupling constant on the nucleus of trico-ordinated nitrogen in the relatively rigid bicyclic diaziridinyls (**13**)–(**15**) by comparison with the monocyclic compounds (**6**)–(**10**) which have a flattened nitrogen pyramid. However, a decrease in spin density on this atom, caused by the weakened n_N–p_N interaction, seems to compensate for the effect of the growing s character of the n_N orbital, and for bicycles (**13**)–(**15**) the hyperfine splitting actually observed on the nucleus of the trico-ordinated nitrogen atom is smaller than in monocyclic diaziridinyls (**6**)–(**10**) (Table 2).

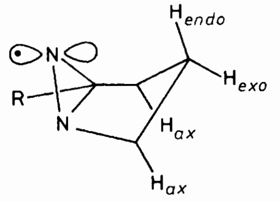
According to the ESR spectra of diaziridinyls (**6**)–(**9**), under conditions of slow nitrogen inversion, stereospecific a_H and a_F constants are observed (Table 2). It can be assumed that these constants are caused by hyperfine splitting with CH_3 and CF_3 groups at C(3) which are *trans*-oriented with respect to the N(2)-substituent since, because of the steric repulsion between the *cis*-group and the N(2)-substituent, the torsion angle φ_1 between the C(3)–C_{cis} bond and the semioccupied p orbital must increase, and, correspondingly, the hyperfine splitting must decrease (Scheme 5).



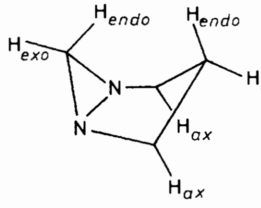
Scheme 5.

In the bicyclic diaziridinyl (**13**) an increase in the φ_2 torsion angle is facilitated by the inclusion of C(5) into the bridgehead of the bicyclic system, and so the a_F constant is not observed.

Based on the values of a_H for bicyclic diaziridinyls (**13**)–(**15**) one can assume that the boat-like conformation is predominant. Indeed, the larger a_H constant can be assigned to the splitting through space on the *endo*-proton at C(3) and the smaller a_H to the splitting through bonds on two axial protons at C(2) and C(4) on 'W' and on one *exo*-proton at C(3) on the 'dipper'.



(13)–**(15)**



(16)

A similar situation was observed by us earlier[14] by ^1H NMR spectroscopy in the case of stereochemically similar 1,5-diazabicyclo[3.1.0]hexanes of type (**16**). For these compounds in a boat-like conformation, we observed a ^4J spin coupling constant of the *exo*-proton at C(6) with the axial protons at C(2) and C(4), as well as ^5J of the *exo*-proton at C(6) with the *exo*-proton at C(3).

Conclusions

The diaziridinyls studied in the present work are the first neutral hydrazyl radicals for which the pyramidal configuration of trico-ordinated nitrogen has been rigorously proved. Four-electron destabilization of the GS and, mainly, three-electron stabilization of the TS of diaziridinyl inversion sharply lowers the barrier, as compared with the corresponding diaziridines. Taking the value of $\Delta\Delta G^{\ddagger}_{\text{inv}} = 67$–$79$ kJ mol^{-1} for the diaziridine/diaziridinyl pair one can assume a planar—or effectively planar on the ESR time scale—configuration of trico-ordinated nitrogen in neutral hydrazyls, corresponding to which are hydrazines with an inversion barrier of 46–50 kJ mol^{-1}. The calculated value of the inversion barrier (25.1 kJ mol^{-1}) of the simplest hydrazyl (**2**), published earlier,[3] is obviously an overestimation.

The bicyclic diaziridinyls (**13**)–(**15**), as well as their precursors (*exo*-6-chloro-1,6-diazabicyclo[3.1.0]hexanes),[15] predominantly exist in the boat-like conformation. Thus, the presence of an unpaired electron at N(6) has practically no effect on the conformational equilibrium of these bicycles.

Experimental

ESR spectra were obtained by irradiation (1 kW, Hg-vapour high pressure lamp) of diaziridine solutions in the cavity of a Varian E-12A spectrometer.

Materials.—1,3,3-Trimethyldiaziridine,[16] *N*-substituted 3,3-bis(trifluoromethyl)diaziridines,[17] 1-methyl-3,3-bis(methoxycarbonyl)diaziridine[18] and 5-substituted *exo*-6-chloro-1,6-diazabicyclo[3.1.0]hexanes[15] were prepared by published methods.

Molecular Orbital Calculations.—The geometries of the ground and transition structures for the inversion of diaziridinyl (**5**) were optimized by gradient methods at the unrestricted Hartree–Fock (UHF) level using the 3-21G split valence basis set.[19] The computations were performed using the GAUSSIAN 80 series of programs.[20]

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