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# SOME 1,2-DIALKYL-1,2-DIARYLHYDRAZINE RADICAL CATIONS, A CONTRIBUTION TO THE GEOMETRY OF HYDRAZINE RADICAL CATIONS

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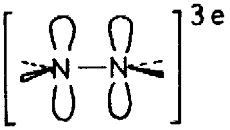
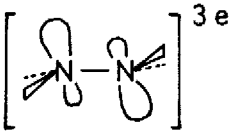
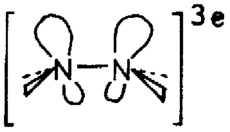
When an electron is removed from a hydrazine system, one expects in the formed hydrazine radical cation considerable flattening at the nitrogens. Three geometries are in discussion for hydrazine radical cations, the planar structure 1a$^{\cdot+}$ 1-4), the staggered anti one 1b$^{\cdot+}$ 3), and the syn eclipsed one 1c$^{\cdot+}$ 4). We wish to report esr results, which are in support for a planar or nearly planar structure like 1a$^{\cdot+}$, at least for the studied aryl-substituted hydrazine radical cations.



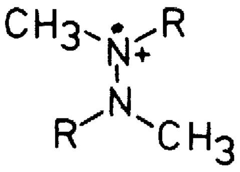
1a$^{\cdot+}$



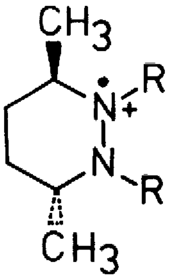
1b$^{\cdot+}$



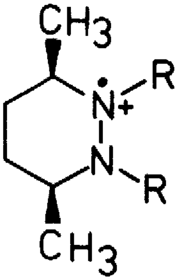
1c$^{\cdot+}$



2$^{\cdot+}$



3$^{\cdot+}$



4$^{\cdot+}$

R = 3,5-di-tert-butylphenyl

Oxidation of the hydrazines 2, 3 and 4 [5)] in acetone/trifluoroacetic acid or in methylene chloride/trifluoroacetic acid with lead tetraacetate yielded the corresponding violet hydrazine radical cations, the esr spectra of which were recorded under stationary conditions. The well resolved esr spectrum of $\underline{2}^{\cdot +}$ at $-20^{\circ}$ consists of 11 groups of lines and was analyzed for $a(N) = 10.80$ G (2N), $a(H_{CH_3}) = 11.65$ (6H), $a(H_{o,o',p}) = 1.67$ (6H); $g = 2.0033$. o- and p-hydrogens are found to be equivalent within the linewidth of 0.2 G. The esr spectrum of the cyclic trans species $\underline{3}^{\cdot +}$ (figure 1) shows only 5 groups of 7 lines yielding $a(N) = 8.75$ G (2N),

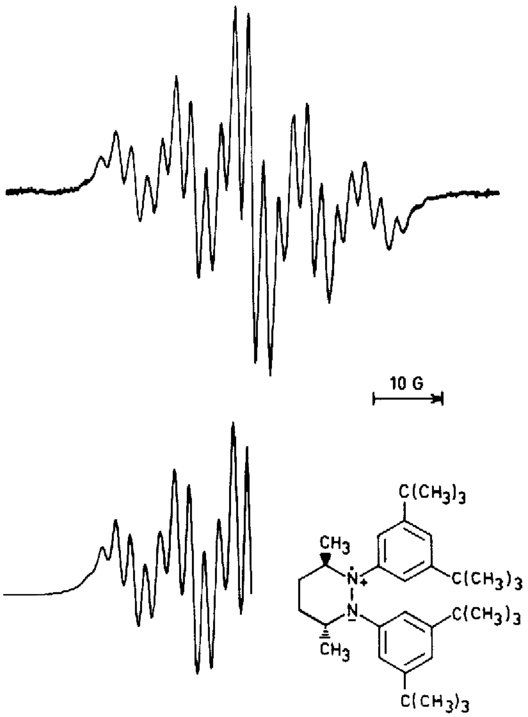


Figure 1. Esr spectrum of $\underline{3}^{\cdot +}$ in methylene chloride/trifluoroacetic acid (20:1) at $-20^{\circ}$C and its simulation (linewidth 1.6 G).

$a(H_{o,o',p}) = 2.1$ (6H); $g = 2.0033$. The two single ß-hydrogens of $\underline{3}^{\cdot +}$ do not show up in the hyperfine structure. Deuteration of these hydrogens leaves the esr spectrum unchanged, even in the linewidth, and there is also no significant change with temperature between $-60^{\circ}$ and $70^{\circ}$C. Therefore one can assume the ß-hydrogen splitting to be smaller than 1 G. The room temperature esr spectrum of the corresponding cis species (figure 2) yielded $g = 2.0034$; $a(N) = 9.60$ G (2N), $a(H_{o,o',p}) = 1.85$ (6H), and an additional extraordinary large splitting "$a(H) = 21.0$ (1H)". This esr spectrum, however, is temperature dependent.

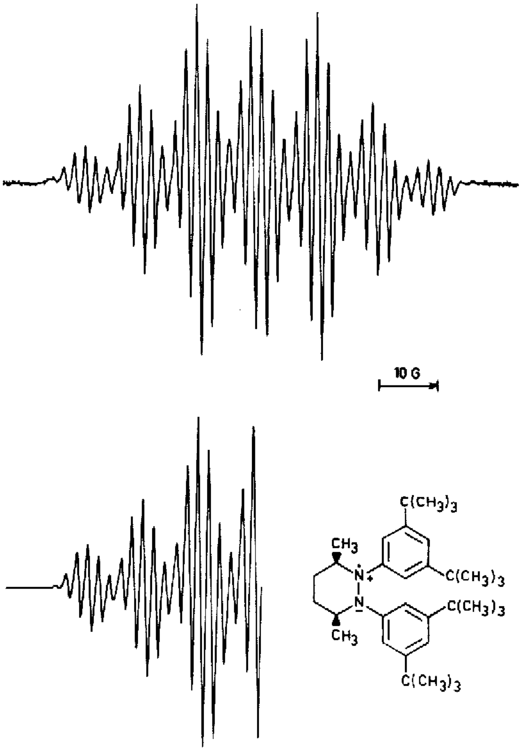
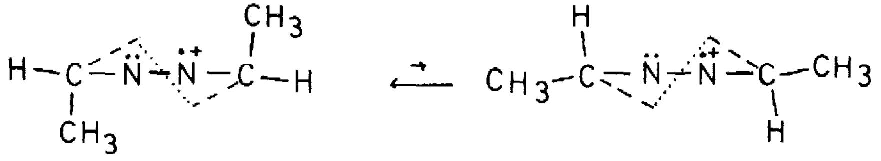


Figure 2. Esr spectrum of $\underline{4}^{\cdot+}$ in methylene chloride/trifluoroacetic acid (20:1) at -20°C and its simulation (linewidth 0.6 G).

At 60°C an additional group of lines starts to show up in the center of the spectrum indicating that the two ß-hydrogens of $\underline{4}^{\cdot+}$ exchange rapidly their conformational positions, $a(H_{average}) = 10.50$ G, obviously by a ring inversion, which might be combined with a simultaneous nitrogen inversion.

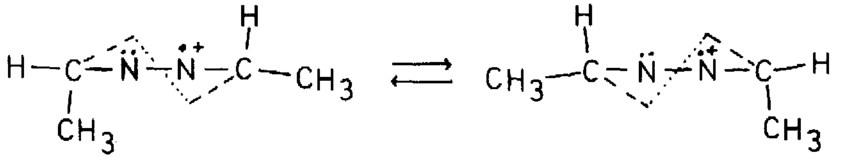
Considering that the hydrazinium system is flat, the cyclic species $\underline{3}^{\cdot+}$ and $\underline{4}^{\cdot+}$ would exist in the equilibrating half chair conformations $\underline{a}$ and $\underline{b}$. In the cis species $\underline{4}^{\cdot+}$ the observed ß-hydrogen splitting would be the average of that for a pseudoaxial and a pseudoequitorial hydrogen. Both conformations, $\underline{4a}^{\cdot+}$ and $\underline{4b}^{\cdot+}$, are of equal energy. This is not the case for the trans compound $\underline{3}^{\cdot+}$. According to the esr spectrum the conformation $\underline{3a}^{\cdot+}$ is predominantly populated, in which the ß-hydrogens occupy pseudoequitorial positions. In $\underline{3}^{\cdot+}$ the large aryl substituents force the methyl groups into the pseudoaxial positions and overcome the 1,3-dipseudoaxial $CH_3$-H interactions of $\underline{3a}^{\cdot+}$. Since the splitting of the pseudoequitorial ß-hydrogens in $\underline{3a}^{\cdot+}$ is smaller than 1 G, most of the 21 G splitting observed in the esr spectrum of $\underline{4}^{\cdot+}$ corresponds to the splitting of the pseudoaxial ß-hydrogen in $\underline{4}^{\cdot+}$.

$3a^{\cdot+}$



$3b^{\cdot+}$

$4a^{\cdot+}$



$4b^{\cdot+}$

The esr results of $\underline{3}^{\cdot+}$ and $\underline{4}^{\cdot+}$ are in agreement with a planar or nearly planar geometry of the hydrazinium system in arylsubstituted hydrazine radical cations, although we cannot definitely exclude a staggered anti conformation $\underline{1b}^{\cdot+}$ of slightly pyramidal nitrogens.

## Acknowledgement

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