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RADICAL CATIONS OF 1,2,4,5-TETRAKIS(DIMETHYLAMINO)BENZENE AND 2,3,6,7-TETRAKIS(DIMETHYLAMINO)NAPHTHALENE: AN ESR AND ENDOR STUDY

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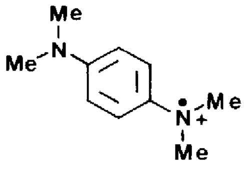
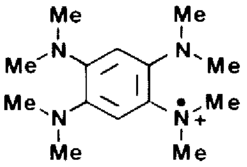
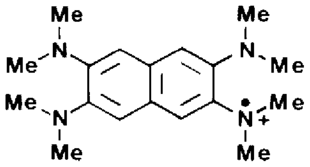
Abstract: The title radical cations, **2**$^{\cdot+}$ and **3**$^{\cdot+}$, were generated by oxidation of the parent compounds with tris(4-bromophenyl)aminium hexachloroantimonate, iodine or lead tetraacetate, and were characterized by ESR and ENDOR. For **2**$^{\cdot+}$ a restricted rotation about the C(aryl)–N bond is found at low temperature ($\leq$ 230 K). The remarkably low $a(\mathrm{H}^{\mathrm{CH}_3})/a(\mathrm{N})$ ratios of **2**$^{\cdot+}$ and **3**$^{\cdot+}$ point to an increase in the average degree of bending at nitrogen.

Synthetic work on compounds with dimethylamino groups in close spatial proximity ("proton sponges") [1] and on new electron donors provided 1,2,4,5-tetrakis(dimethylamino)benzene (**2**) [2] and 2,3,6,7-tetrakis(dimethylamino)naphthalene (**3**).[3] The corresponding radical cations **2**$^{\cdot+}$ and **3**$^{\cdot+}$ are related to the well known Wurster's blue radical cation **1**$^{\cdot+}$ [4,5] which should have a definite barrier to rotation about the C–N(CH$_3$)$_2$ bond, as found in arylamine radical cations [6] and in the tetrakis(dimethylamino)ethene radical cation.[7a] **2**$^{\cdot+}$ and **3**$^{\cdot+}$ may present experimental evidence of this restricted rotation, since their methyl groups have different environments corresponding to *endo* and *exo* arrangements of CH$_3$ in the adjacent N(CH$_3$)$_2$ substituents.


1$^{\cdot+}$


2$^{\cdot+}$


3$^{\cdot+}$

The cyclovoltammogram of **2** in acetonitrile showed instead of the expected separated oxidation steps for the formation of **2**$^{\cdot+}$ and **2**$^{2+}$ an apparent two electron oxidation step.[2] In agreement with this finding oxidation of **2** with iodine in acetonitrile readily afforded the diamagnetic **2**$^{2+}$ I$^-\cdot$I$_3^-$ salt as deep violet crystals.[2] Comproportionation of **2**$^{2+}$ and **2** in acetonitrile generated **2**$^{\cdot+}$ only in traces (identified by ESR). All these observations indicate that **2**$^{\cdot+}$ in acetonitrile undergoes a fast disproportionation to give **2** and **2**$^{2+}$. Therefore other generation procedures for **2**$^{\cdot+}$ had to be investigated. The radical cations **2**$^{\cdot+}$ and **3**$^{\cdot+}$ were prepared by electron transfer to tris(4-bromophenyl)aminium hexachloroantimonate (TBPA) in ethanol/dichloromethane (4:1). Using this method (A) the ESR spectra of **2**$^{\cdot+}$ [Fig. 1(a)] and **3**$^{\cdot+}$ can be recorded at room temperature. Oxidation with iodine in dichloromethane also generated **2**$^{\cdot+}$ and **3**$^{\cdot+}$ (method B); **2**$^{\cdot+}$ was identified by its low temperature (230 K) ESR spectrum and **3**$^{\cdot+}$ by the ^{1}H ENDOR spectrum. Under these conditions, however, the lifetime of the radical cations is considerably shorter. **3**$^{\cdot+}$ was also detected by reacting **3** with lead tetraacetate in dichloromethane (method C; Fig. 2).

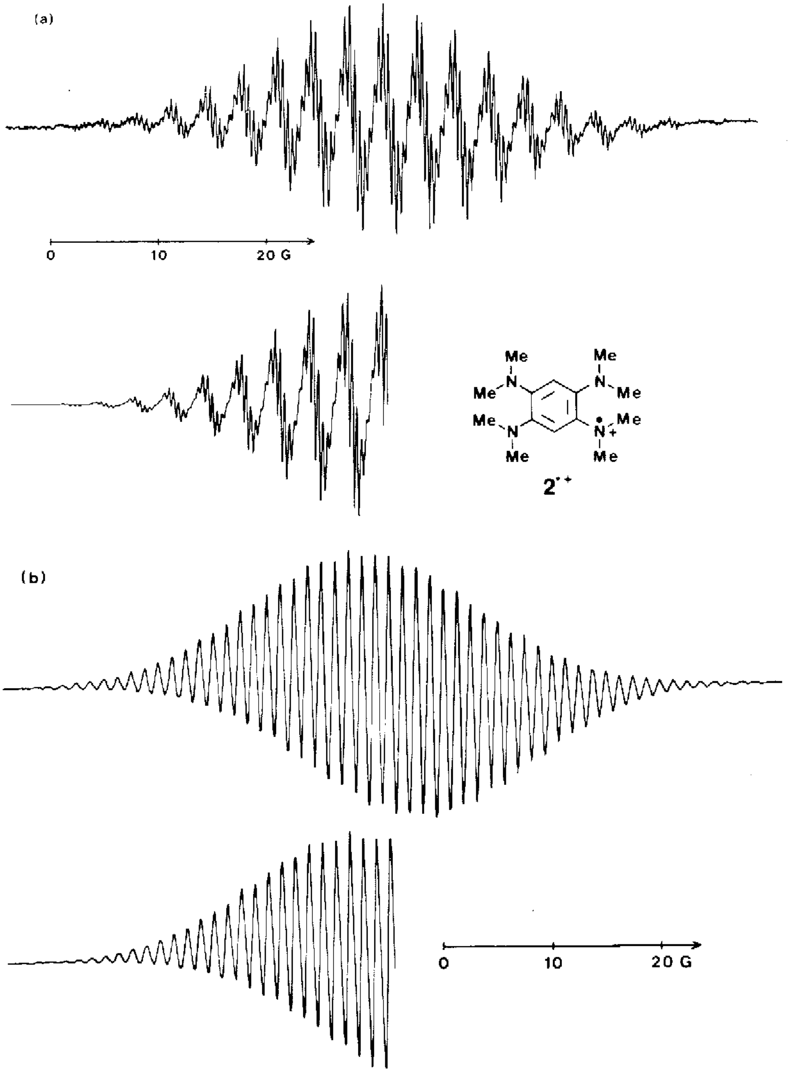


Fig. 1: ESR spectra for $2^{\bullet +}$ in ethanol/dichloromethane (4:1) together with half-spectra simulations using the data given in Table 1: (a) at 298 K, (b) at 220 K.

Table 1. Isotropic hyperfine coupling constants for $2^{\bullet +}$ and $3^{\bullet +}$.

		Method	Temperature/K	a(N)/G [a]	$a(\mathrm{H}^{\mathrm{CH_3}})$/G [b]	a(H)/G [c]	g-Value
$2^{\bullet +}$	ESR	A	298	3.57	3.13	0.42 [d]	2.0031
	ESR	A	220	3.65	3.76, 2.56	0.34	
	ENDOR	A	245	3.64	3.15		
	ENDOR	A	220		+3.76, +2.56	+0.34	
	ESR	B	230	3.65	3.75, 2.60	0.35	2.0031
$3^{\bullet +}$	ESR	A	298	3.15	2.81	0.88	2.0030
	ENDOR	A	220		+2.84	-0.88	
	ENDOR	B	230		+2.84	-0.72	
	ESR	C	230	3.21	2.84	0.72	2.0030

[a] 4N. [b] 12 + 12H. [c] $2^{\bullet +}$: 2H; $3^{\bullet +}$: 4H. [d] Or 0.85 G, see text.

In all performed generation procedures $\mathbf{2}^{\cdot +}$ always turned out to be less persistent than $\mathbf{3}^{\cdot +}$. Method B (E_{ox} = 0.535 V) and the aforementioned comproportionation of **2** and $\mathbf{2}^{2+}$ in acetonitrile assure that mono radical cations are generated.

The analysis of the ESR spectra is substantially facilitated by the ENDOR studies. In the ENDOR spectra all ^{1}H coupling constants were clearly detected, in case of $\mathbf{2}^{\cdot +}$ also the ^{14}N signals, and, in addition, by performing general triple resonance experiments [8] relative signs were determined. a(N) and a(H^{CH_3}) are considered to be positive. The latter was taken as reference for the further sign assignments. The resolved ESR spectra (Fig. 1 and 2) are well simulated with the values given in Table 1. There is only some ambiguity regarding $a(H^{3,6})$ of $\mathbf{2}^{\cdot +}$. The 298 K ESR spectrum of $\mathbf{2}^{\cdot +}$ can equally well be simulated by using a($H^{3,6}$) = 0.85 G. We cannot exclude this possibility, because the $a(H^{3,6})$ splitting was not detectable in the 245 K ENDOR spectrum of $\mathbf{2}^{\cdot +}$.

The ESR [Fig. 1(b)] and ENDOR spectra of $\mathbf{2}^{\cdot +}$ at 220 K yield two sets of methyl proton splittings, $a(H^{CH_3})$ = 3.76 (12H) and $a(H^{CH_3})$ = 2.56 G (12H), which average above 245 K due to rapid interconversion of the *exo* and *endo* methyl groups, a(H^{CH_3}) = 3.15 G (24H). In case of $\mathbf{3}^{\cdot +}$, this restricted rotation about the C(aryl)–N bond was not observed in the studied temperature range.

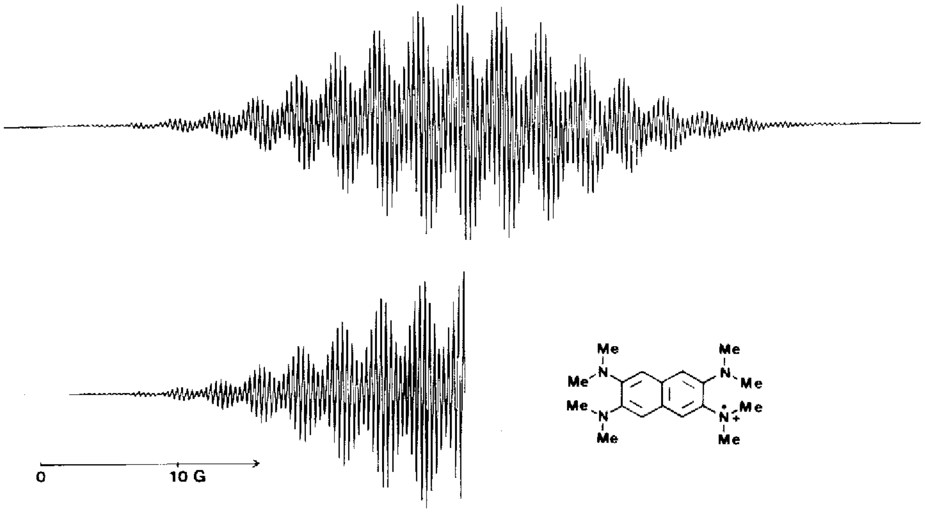
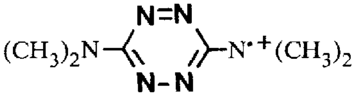


Fig. 2. ESR spectrum for $\mathbf{3}^{\cdot +}$ in dichloromethane at 230 K together with the half-spectrum simulation using the data given in Table 1.

ESR data of various radical cations with R–$N^{\cdot +}(CH_3)_2$ structures, compiled in Table 2, indicate that the $a(H^{CH_3})/a(N)$ ratio may be sensitive to the charge density on nitrogen. $\mathbf{1}^{\cdot +}$ and the 3,6-bis(dimethylamino)-1,2,4,5-tetrazine radical cation, in which the positive charge is mainly localized on the two dimethylamino functions, can be regarded to be derivatives of the tetramethylhydrazine radical cation. In this series the radical cation with the electron-withdrawing 1,2,4,5-tetrazine bridge shows some increase of the $a(H^{CH_3})/a(N)$ ratio. The value of 1.08 agrees well with that of the N,N-dimethylphenylamine radical cation (1.07).[10] In $\mathbf{2}^{\cdot +}$ and $\mathbf{3}^{\cdot +}$ the positive charge is delocalized onto four dimethylamino groups. For these radical cations a decrease of $a(H^{CH_3})/a(N)$ is observed, the mean value being *ca.* 0.88. The

$a(\mathrm{H}^{\mathrm{CH}_3})/a(\mathrm{N})$ ratio depends on the average geometry at the nitrogen centre.13) Large $a(\mathrm{H}^{\mathrm{CH}_3})/a(\mathrm{N})$ ratios indicate a planar $\mathrm{N}^{\bullet+}$ geometry, e. g. 1.78 for $(\mathrm{CH}_3)_2\mathrm{NH}^{\bullet+}$. The $a(\mathrm{H}^{\mathrm{CH}_3})/a(\mathrm{N})$ ratio decreases when the planar geometry is destabilized, for instance by steric effects. Therefore the lower $a(\mathrm{H}^{\mathrm{CH}_3})/a(\mathrm{N})$ ratios of $\mathbf{2}^{\bullet+}$ and $\mathbf{3}^{\bullet+}$, and particularly that of the tetrakis(dimethylamino)ethene radical cation (Table 2) point to a relative increase in the average degree of bending at the nitrogen centre.13) For dimethylamino functions with different $a(\mathrm{H}^{\mathrm{CH}_3})$ coupling constants it has been suggested 7a,b) that the methyl group showing the lower $a(\mathrm{H}^{\mathrm{CH}_3})/a(\mathrm{N})$ ratio is the more sterically hindered one. Taking up this point the smaller methyl proton splitting of $\mathbf{2}^{\bullet+}$, $a(\mathrm{H}^{\mathrm{CH}_3})$ = 2.56 G, may represent the *endo* methyl groups.

Table 2. $a(\mathrm{H}^{\mathrm{CH}_3})$, $a(\mathrm{N})$ and $a(\mathrm{H}^{\mathrm{CH}_3})/a(\mathrm{N})$ data for radical cations with $\mathrm{R{-}N}^{\bullet+}(\mathrm{CH}_3)_2$ structures.

	$a(\mathrm{H}^{\mathrm{CH}_3})/\mathrm{G}$	$a(\mathrm{N})/\mathrm{G}$	$a(\mathrm{H}^{\mathrm{CH}_3})/a(\mathrm{N})$	Lit.
$\mathrm{N}^{\bullet+}(\mathrm{CH}_3)_3$	28.56	20.55	1.39	9)
$\mathrm{H}_5\mathrm{C}_6\mathrm{N}^{\bullet+}(\mathrm{CH}_3)_2$	11.8	11.0	1.07	10)
$(\mathrm{CH}_3)_2\mathrm{N{-}N}^{\bullet+}(\mathrm{CH}_3)_2$	12.61	13.38	0.94	11)
	8.75	8.09	1.08	12)
$\mathbf{1}^{\bullet+}$	6.76	6.99	0.97	5a)
$\mathbf{2}^{\bullet+}$	3.76	3.57	1.03	
	2.56		0.70	
$\mathbf{3}^{\bullet+}$	2.81	3.15	0.89	
$[(\mathrm{CH}_3)_2\mathrm{N}]_2\mathrm{C{=}C}[\mathrm{N}(\mathrm{CH}_3)_2]\mathrm{N}^{\bullet+}(\mathrm{CH}_3)_2$	3.28	4.90	0.67	7b)
	2.84		0.58	

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