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Radical Cations of 1,2-Bis(dialkylamino)benzenes: Restricted Rotation about the C–NMe$_2$ Bond

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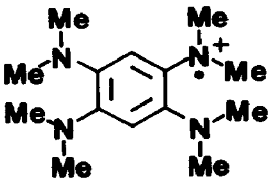
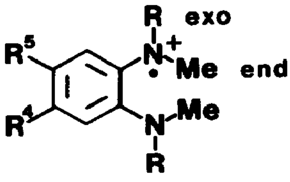
Abstract: The 1,2-bis(dialkylamino)benzene radical cations **2a**–**c**$^{\bullet+}$ were generated by oxidation of the parent compounds with iodine or lead tetraacetate. ESR and ENDOR studies of **2a**$^{\bullet+}$ and **2b**$^{\bullet+}$ gave evidence of a restricted rotation about the C–NMe$_2$ bond; based on the results of **2c**$^{\bullet+}$ the different N-methyl proton splittings in **2a**$^{\bullet+}$ and **2b**$^{\bullet+}$ were assigned to the *exo* and *endo* N-methyl groups.

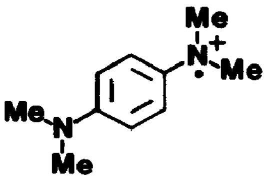
Experimental evidence of a restricted rotation about the C–NMe$_2$ bond has been found for various amine radical cations, e.g. arylamine radical cations[1], the tetrakis(dimethylamino)ethene radical cation[2], the 1,2,4,5-tetrakis(dimethylamino)benzene radical cation (**1**$^{\bullet+}$),[3] and the 1,4,5,8-tetrakis(dimethylamino)-naphthalene radical cation.[4] In context with the ESR study of **1**$^{\bullet+}$ we became aware that the radical cation of 1,2-bis(dimethylamino)benzene (**2a**$^{\bullet+}$), the ortho-substituted isomer of the well known Wurster's blue radical cation **3**$^{\bullet+}$,[5,6] has not been observed by ESR, although it has been clearly detected by cyclovoltammetry.[7] In the case of **2a**$^{\bullet+}$ too, a restricted rotation about the C–NMe$_2$ bond can be expected which would lead to different environments of the N-methyl groups corresponding to *endo* and *exo* arrangements of CH$_3$ in the adjacent NMe$_2$ substituents.



1$^{\bullet+}$



2a$^{\bullet+}$: R = Me, R^4 = R^5 = H
2b$^{\bullet+}$: R = R^4 = R^5 = Me
2c$^{\bullet+}$: R = CHMe$_2$, R^4 = R^5 = H



3$^{\bullet+}$

For dimethylamino groups with different a(H–NCH$_3$) coupling constants it has been suggested[2a,b] that the methyl group yielding the lower a(H–NCH$_3$)/a(N) ratio is the more sterically hindered one, and, hence, should represent the *endo* methyl group. The argument for this assignment comes from ESR studies of selectively *cis*- or *trans*-methyl substituted allyl radicals which have unambiguously shown the *endo* (*cis*) methyl proton splitting to be smaller than the *exo* (*trans*) one, e. g. 14.0 G versus 16.4 G.[8,9] Since various properties of allyl radicals differ basically from those of amine radical cations, a further point of our concern was to verify the suggested *endo* and *exo* N–CH_3 assignment in radical cations of type **2**$^{\bullet+}$ by experimental evidence. A promising test compound is the radical cation **2c**$^{\bullet+}$. In **2c**$^{\bullet+}$ the more space-requiring 2-propyl substituents should occupy the *exo* positions.

The precursor compounds 1,2-bis(dimethylamino)benzene (**2a**)[10] and 1,2-bis(dimethylamino)-4,5-dimethylbenzene (**2b**)[7] were prepared following the literature procedures. 1,2-Bis(N-methyl-2-propylamino)-benzene (**2c**) was obtained in three steps: Formylation of 1,2-diaminobenzene with acetic formic anhydride in trichloromethane afforded in high yield (95%) 1,2-bis(formylamino)benzene[11] which was reduced with lithium aluminum hydride to give 1,2-bis(methylamino)benzene.[11,12] Subsequent alkylation with 2-propyl iodide in the presence of potassium hydroxide in dimethylformamide provided **2c** as colourless oil (59% yield based on 1,2-bis(formylamino)benzene).

Oxidation of **2a** and **2c** with iodine and of **2b** with lead tetraacetate in dichloromethane generated the corresponding radical cations which are rather shortlived. Therefore generation, and ESR and ENDOR studies had to be carried out at about 200 K.

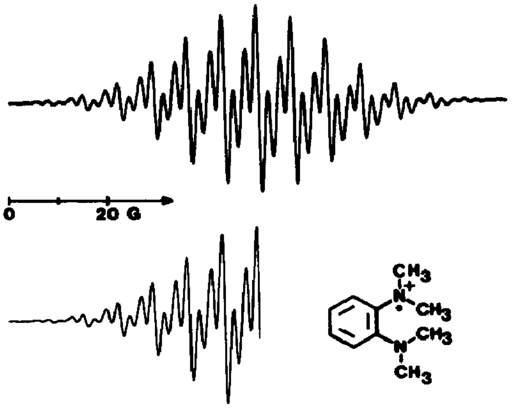


Fig. 1. ESR spectrum of **2a**$^{\bullet+}$ in dichloromethane at 200 K together with a simulation using the data given in Table 1.

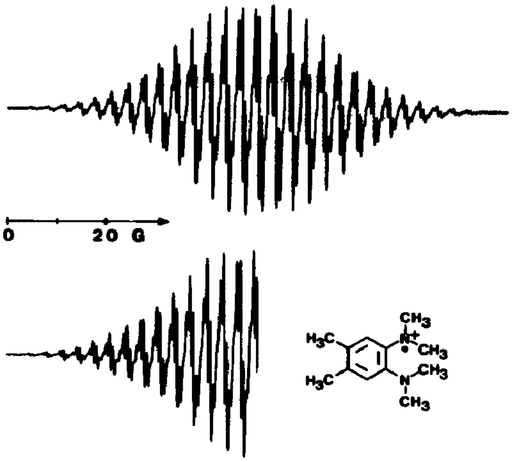


Fig. 2. ESR spectrum of **2b**$^{\bullet+}$ in dichloromethane at 225 K together with a simulation using the data given in Table 1.

The ESR spectrum of **2a**$^{\bullet+}$ (Fig.1) is only partially resolved. ENDOR, however, revealed clearly two different N-methyl hydrogen coupling constants, 7.17 and 6.77 G, and a further hydrogen splitting of 2.21 G related to aryl hydrogens. Based on these results the simulation of the ESR spectrum provided the nitrogen coupling constant and showed that two hydrogens give rise to the a(H) = 2.21 G splitting. Their positions could be determined by selective methyl substitution. Simulation of the considerably better resolved ESR spectrum of the 4,5-dimethyl substituted **2b**$^{\bullet+}$ (Fig.2) using the obtained ENDOR data (Table 1) shows clearly that the a(H) = 3.27 G splitting stems from the six methyl hydrogens. Consequently the a(H) = 2.21 G splitting of **2a**$^{\bullet+}$ has to be assigned to the 4,5-hydrogens. The two different

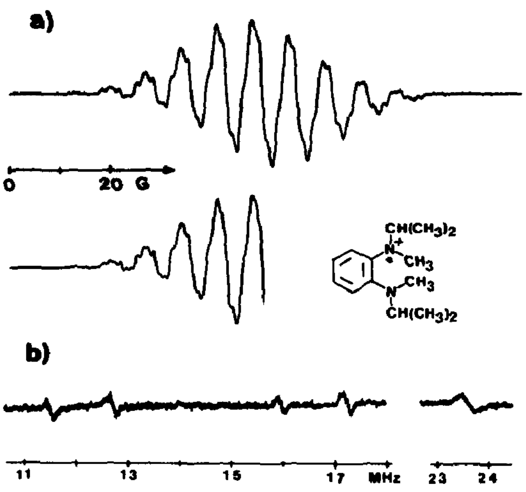


Fig. 3. a) ESR-spectrum of **2c**$^{\bullet+}$ in dichloromethane at 225 K together with a simulation using the data given in Table 1; b) ENDOR spectrum of **2c**$^{\bullet+}$ in dichloromethane at 180 K.

Table 1. Isotropic Hyperfine Coupling Constants and *g*-Values of **2a–c**$^{\bullet+}$ in Dichloromethane.

	Method	*T*/K	*a*(N)/G	*a*(H-NCH$_3$)/G	*a*(H)[R^4,R^5]/G	*a*(H)/G	*g*-Value
2a$^{\bullet+}$	ESR	200	6.95 (2N)	7.19 (6H)	2.22 (2H)		2.0031
				6.78 (6H)			
	ENDOR	180		7.17	2.21		
				6.77			
2b$^{\bullet+}$	ESR	225	6.58 (2N)	6.77 (6H)	3.37 (6H)		2.0031
				6.09 (6H)			
	ENDOR	180		6.75	3.37		
				6.09			
2c$^{\bullet+}$	ESR	200	7.12 (2N)	6.65 (6H)	2.03 (2H)	1.17 (2H)[a]	2.0031
	ENDOR	180		6.65	2.03	1.17	

[a] Splitting represents the CH proton in the 2-propyl group.

N-methyl hydrogen coupling constants of **2a**$^{\bullet+}$: *a*(H-NCH$_3$) = 7.17 and 6.77 G [*a*(H-NCH$_3$)/*a*(N) = 1.03 or 0.97], and of **2b**$^{\bullet+}$: *a*(H-NCH$_3$) = 6.75 and 6.09 G [*a*(H-NCH$_3$)/*a*(N) = 1.03 or 0.93] are proof of a restricted rotation about the C–NMe$_2$ bond and represent N-methyl groups in *exo* or *endo* arrangement.

In order to achieve an experimental *endo*/*exo* assignment **2c**$^{\bullet+}$ was studied. Its ENDOR spectrum (Fig. 3b) provided clearly the presumed three large hydrogen splittings, while the *a*(3,6-H) and *a*(H-CCH$_3$) splittings, expected to be very small, were not detectable. Based on the simulation of the ESR spectrum (Fig. 3a) also the nitrogen splitting could be determined. The similar *a*(N) and *a*(4,5-H) coupling constants of **2c**$^{\bullet+}$ and **2a**$^{\bullet+}$ (Table 1) show that the spin density distribution and, consequently, the planarization about the

C(aryl)–N bond are not significantly affected by the N–(2-propyl) substitution. Together with the small $a(\text{H-NCH}_3)/a(\text{N}) = 0.93$ ratio[3] this can be taken as evidence that also in $\mathbf{2c}^{\bullet+}$ there is a restricted rotation about the C(aryl)–N bond in the studied temperature range. Spatial requirements force the large N(2-propyl) groups to occupy the *exo* positions. Therefore the N-methyl hydrogen splitting of $\mathbf{2c}^{\bullet+}$ with the low $a(\text{H-NCH}_3)/a(\text{N}) = 0.93$ ratio reflects *endo* N-methyl groups. In accordance with the results of substituted allyl radicals,[8,9] in amine radical cations of type $\mathbf{2}^{\bullet+}$ and presumably also in the other cited examples[2-4] the N-methyl groups showing the relatively smaller $a(\text{H-NCH}_3)$ splitting are the more sterically hindered ones and represent *endo* N-methyl groups.

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    All compounds gave satisfactory elemental analyses. 1,2-Bis(formylamino)benzene: colourless crystals from ethanol, m. p. 171–172 °C, yield 95%; $m/z = 164$ (100%, M$^+$). 1,2-Bis(methylamino)benzene:[12] oil; ^{1}H-NMR (360 MHz, [D$_6$]DMSO): $\delta = 6.56$ (m, 2H, Ar–H), 6.40 (m, 2H, Ar–H), 4.52 (q, ^3J = 5.0 Hz, 2H, NH), 2.68 (d, 6H, NCH$_3$). 1,2-Bis(N-methyl-2-propylamino)benzene (purified by column chromatography; alumina, hexane): colourless oil, b. p. 85–86 °C/0.15 mbar, yield 59% based on 1,2-bis(formylamino)benzene; ^{1}H-NMR (360 MHz, [D$_6$]DMSO): $\delta = 6.88$ (m, 4H, Ar–H), 4.06 (sep, ^3J = 6.6 Hz, 2H, NCH), 2.55 (s, 6H, NCH$_3$), 0.98 (d, 12H, CCH$_3$); MS: $m/z = 220$ (100%, M$^+$).
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