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Comment on „Synthesis, Characterization, and Structures of a Persistent Aniline Radical Cation“: A New Interpretation Is Necessary**

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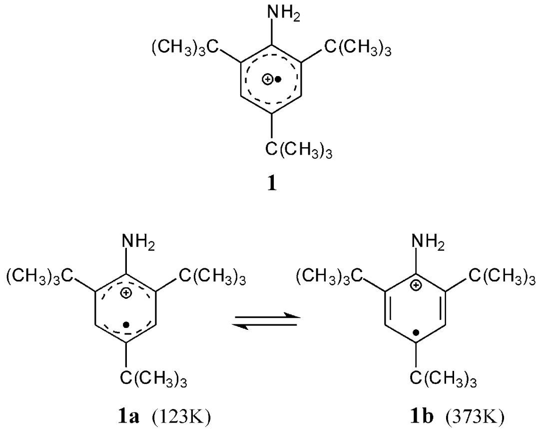
anilines · radical cations · structure elucidation

In their recent Communication,[1] Chen et al. reported on the „Synthesis, Characterization, and Structures of a Persistent Aniline Radical Cation“. After oxidation of 2,4,6-tri-*tert*-butylaniline (TBA) with $AgSbF_6$ in dichloromethane the authors isolated a green, crystalline compound which they identified, based on UV/Vis and ESR spectrometric data, as the hexafluoroantimonate salt of the TBA radical cation, $TBA^{\bullet +}SbF_6^-$ (**1**) (Scheme 1). Single-crystal X-ray analysis of the green compound at 123 K revealed an unsually long C_{Ar}–N bond length of 1.496 Å. Such a bond length could not be reproduced by ab initio and density functional theory (DFT) quantum-chemical calculations of the isolated $TBA^{\bullet +}$ molecule. Only when two SbF_6^- anions were incorporated in the computations did an ab initio (MP2) method predict a similarly long C–N bond of 1.498 Å. Most remarkably, with increasing temperature the X-ray data indicated a dramatic, reversible change of the geometry of the phenyl ring of $TBA^{\bullet +}$. At 373 K, the longitudinal C2–C3/C5–C6 bonds were contracted from 1.423 Å at 123 K to an unusually short length of 1.281 Å, but the C_{Ar}–N bond length remained almost unchanged. These variations of geometry were attributed to a Jahn–Teller effect, the interchange of a low-temperature bisallyl structure (**1a**) and a high-temperature quinoid structure (**1b**) (Scheme 1).



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1a (123K)

1b (373K)

Scheme 1.

In fact, the presence of $TBA^{\bullet +}$ in the isolated compound is evidenced by its green color and some ESR data. Close inspection of the data presented in Ref. [1], however, casts serious doubts on the identification of the green solid as the *stoichiometrically pure* $TBA^{\bullet +}SbF_6^-$ radical cation salt. Also, the interpretation of the temperature-dependent structural changes in terms of a Jahn–Teller distortion appears to be highly ambiguous. My lines of reasoning, supported by DFT calculations, are as follows.

ESR Spectrometry

1. An ESR spectrum attributed to $TBA^{\bullet +}$, obtained from a 10^{-4} M dichloromethane solution of the green compound, is shown in Figure 2 of Ref. [1]. Unfortunately, instrument settings were not given either in the paper or in its Supporting Information; thus, the choice of suitable recording conditions (especially microwave power and modulation amplitude) can only be assumed. On this premise, the spectrum shows a surprisingly high level of noise. For a 10^{-4} M concentration of a *pure* organic radical (cation) exhibiting relatively few, narrow hyperfine lines, a strong, essentially noiseless spectrum can be expected. I thus suspect that the spectrum in Figure 2 of Ref. [1] is due to paramagnetic contaminations (in the lower percentage range) incorporated in a diamagnetic, that is, ESR-silent compound. An estimation of the spin concentration would have easily established this.[2]

2. The authors inferred their assignment of the ESR spectrum to $TBA^{\bullet +}$ from a spectral simulation (Figure 2 of Ref. [1]) with hyperfine splitting constants (hfsc) of $a(^{14}N) = 5.48$ G, $a(N^1H) = 6.62$ G (2 H), and $a(^1H_{meta}) = 2.90$ G (2 H).[3] Reference was given to a paper by Neugebauer et al. where ESR data are reported for a variety of aniline radical cations, but not for $TBA^{\bullet +}$.[4] In fact, the ESR data for $TBA^{\bullet +}$ in nitromethane and trifluoroacetic acid solution have been reported earlier.[5,6] The hfsc given there (see the Supporting

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Information, Table S1) agree well with those of other aniline radical cations[7,8] but differ significantly from the above values. In particular, the significantly smaller *meta*-H hfsc and the resolvable *para-tert*-butyl hydrogen splittings turn out to be very characteristic for alkyl-substituted aniline radical cations. Apart from the known larger deviations for the ^{14}N splittings,[9] the ESR data of TBA$^{\bullet+}$ were very well reproduced by DFT calculations (Table S1), thus demonstrating that the differences in the hyperfine splittings cannot be attributed to solvent and/or counterion effects.

3. In addition, the experimental spectrum in Figure 2 of Ref. [1] clearly shows (note its asymmetry) the presence of at least one additional radical species with a somewhat larger *g* factor but similar overall width. It has been reported that TBA$^{\bullet+}$ decomposes slowly in solution.[10,11] Thus, if one considers the experimental conditions—isolation of „TBA$^{\bullet+}$SbF$_6^-$“ after a reaction period of 24 h at room temperature—the spectrum obviously shows „late“, persistent radical products from the decomposition of TBA$^{\bullet+}$. Reasonably, such radicals might have been produced by partial deprotonation of TBA$^{\bullet+}$ (unreacted TBA serving as a base) to give aminyl radical **2**, and/or radical species deriving from the dimer of **2**, hydrazine **3** (Scheme 2). The latter has been reported to be in equilibrium with **2**.[12] Unfortunately, no *g* factors which would have facilitated the identification of the class of the radicals/radical ions were reported for the solution ESR spectra. The *g* factors of alkyl-substituted aniline radical cations are uniformly in the range of 2.0027–2.0029;[7,8] aromatic aminyl radicals like **2** have *g* factors in the range of 2.0030–2.0036.[13–15] These values also were excellently reproduced by DFT calculations (Tables S1 and S2).

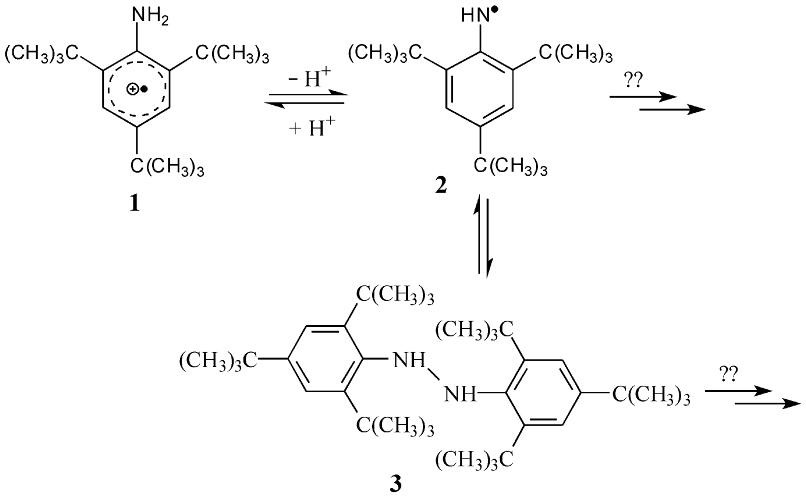
4. A *g* factor of 2.0039 was reported for the solid-state ESR spectrum of the green compound (Figure S2 of Ref. [1]). This value is at odds with the one expected for TBA$^{\bullet+}$ (see above). Note that *g* factors in the range of 2.0037–2.0039 are very typical for hydrazinyl radicals.[13–15] Again, the spin concentration of the green solid had not been determined. The method of choice would have been the measurement of the temperature dependence of the magnetic susceptibility.

5. Without any further comment, ESR spectra of the green compound recorded at 293, 303, and 330 K in acetonitrile solution are displayed in Figure S2 of the Supporting Information of Ref. [1]. Again, two different radicals are clearly visible, but the splitting patterns of these only moderately intense spectra differ strikingly from those in Figure 2 of Ref. [1]. Remarkably, the major spectral component of the „330 K“ spectrum in fact turned out to be essentially identical to the spectrum of TBA$^{\bullet+}$ as displayed in Ref. [3].[16] (The broad linewidth accounts for the unresolved *para-tert*-butyl hyperfine splittings.) Thus, TBA$^{\bullet+}$ is present in the acetonitrile solution of the isolated compound, but again at a substoichiometric level. Note that the splitting pattern of the other spectral component in Figure S2 of Ref. [1], exhibiting a smaller linewidth and a higher *g* factor than TBA$^{\bullet+}$, does not seem to match that of aminyl radical **2** (Supporting Information, Table S2).

UV/Vis Spectrometry

1. In Figure 1 of Ref. [1] TBA$^{\bullet+}$ was further identified by the characteristic UV/Vis absorption at $\lambda_{\max} = 430$ nm.[11,17] However, in line with the conclusions drawn from the ESR experiments, strong absorptions in the 200–350 nm range again indicate the substantial presence of other compounds, as evident from comparison with the experimental UV/Vis spectra and spectra computed by time-dependent DFT (TDDFT) (see Figures S1 and S2 and Ref. [1], Figure S15). Since the absorption coefficient of TBA$^{\bullet+}$ has been reported ($\log \varepsilon_{430\mathrm{nm}} = 3.81$),[11] it is astonishing that the concentration of TBA$^{\bullet+}$ had not been determined.[18,19]

2) Somewhat confusing is the statement that the „…radical character of TBA$^{\bullet+}$ is indicated by the 430 nm absorption…“ (Supporting Information for Ref. [1], p. S17). The radical cationic character is visibly manifested by the characteristic green color, which must be due to absorptions at wavelengths > 700 nm, as has been reported for other



Scheme 2.

aniline radical cations.[11,17] In accord, TDDFT calculations on the UPBE0/6-31G(d) level predict a weak absorption band at $\lambda_{max} = 728$ nm (shifted to ca. 850 nm after correction for the reported average error of TD-PBE0[21]) (Figure S1). Noteworthy, also the UCAM-B3LYP method employed in Ref. [1] (Figure S15) yields a long-wavelength transition (687 nm), which the authors seem to have ignored or overlooked.

Jahn–Teller Distortion

The interpretation of the strong, reversible geometrical changes of the X-ray structures of „TBA$^{\bullet+}$SbF$_6^-$" through a Jahn–Teller (JT) effect (Scheme 1) is hard to comprehend. To my knowledge, a JT distortion must be expected for a high-symmetry structure having a (nearly) degenerate ground state, like the hexafluorobenzene radical cation (C$_6$F$_6^{\bullet+}$) cited by the authors. However, the substitution pattern of TBA$^{\bullet+}$ not only reduces the D_{6h} symmetry of the benzene system significantly (to C_{2v}), but also the electronic effects of the substituents (NH$_2$ vs. *tert*-butyl) are strong enough to lift the degeneracy of the highest occupied molecular orbitals. Although the authors computed the structures of TBA$^{\bullet+}$ on various levels of theory, they obviously did not take into account the orbital energies. Unrestricted (U) und restricted-open (RO) DFT calculations, including CAM-B3LYP, clearly reflect the lifting of the degeneracy of the upper occupied orbitals of TBA$^{\bullet+}$ (Figures S3–S6).

X-Ray Crystallography

1) The X-ray spectroscopic features of the green compound remain mysterious. The exceedingly long C$_{Ar}$−N bond about 1.5 Å in length is unprecedented for aniline-type compounds and could also not be reproduced by theoretical calculations of TBA$^{\bullet+}$ (Ref. [1], Figure 4 and Figures S11 and S12). As the authors noted, „…the experimental geometry of TBA$^{\bullet+}$ can be reproduced only when two SbF$_6^-$ anions are included into calculation (Figure 4b) at the UMP2/6-31G(d) level …",[1] but not by a variety of DFT procedures. Apart from the fact that presenting the single MP2 result as support for the experimental data appears somewhat arbitrary, the calculated MP2 structure shows most benzene C−C bonds to be significantly elongated as well (Ref. [1], Figure 4). The authors did not comment on the obvious contradiction to experiment (Ref. [1], Figure 3 and Figure S9).

2) The authors further state that „…the CN bond (ca. 1.5 Å) basically remains the same length throughout the temperature range…". Based on comparison with the X-ray structure of 2,4,6-tri-*tert*-butylanilinium hexafluoroantimonate (TBAH$^+$SbF$_6^-$) „… any possibility for N-protonation…" was excluded. However, they do not discuss the fact that the bond was found to be contracted to about 1.470 Å at 273–296 K (Ref. [1], Table S2), that is, to the typical lengths of anilinium ions [r(C$_{Ar}$–NH$_3^+$) = (1.466 ± 0.007) Å[22]].[23]

3. The extreme contraction of the C2−C3 and C5−C6 bonds in TBA$^{\bullet+}$SbF$_6^-$ to about 1.281 Å at 373 K is highly unusual. Such a C=C bond is much shorter than those in ordinary alkenes and even allene (sp^2–sp bond, $r = 1.309$ Å). It is hard to imagine that the association of two SbF$_6^-$ anions stretches the C$_{Ar}$−N bond to about 1.5 Å but that this bond length would not be noticeably affected by the apparent strong shortening of the longitudinal benzene bonds at elevated temperatures. Since the quantum-chemical computations fail to explain the solid-state structural changes convincingly, experimental artifacts might be suspected.[24]

In conclusion, the ESR and UV/Vis spectrometric data presented in Ref. [1] do not confirm the green compound as a *stoichiometrically pure* TBA$^{\bullet+}$SbF$_6^-$ salt, the quantum-chemical data do not convincingly support the reported structural data, and the interpretation of the apparent temperature-dependent structural changes in the solid state is open to interpretations other than the Jahn–Teller effect. A careful reexamination of the X-ray data is strongly recommended.

Computational Details

Quantum-chemical computations were performed with the Gaussian 09[25] (geometry optimizations and UV spectra) and ORCA[26] programs (ESR parameters). Orbital graphics were produced with Gabedit.[27]

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[2] The spin concentration can be estimated in a straightforward fashion by recording the solution ESR spectra of a stable radical like TEMPO or diphenylpicrylhydrazl (DPPH) and that of the sample at equimolar concentrations under identical conditions and double integration of both spectra. In our experience, the relative error of this method is about 5–10 %.

[3] No magnetic field scale is shown in Figure 2 of Ref. [1]. It seems that the experimental and simulated spectra were reproduced on somewhat different scales. Otherwise, the simulated spectrum (overall width at line centers, 30.0 G) would not satisfactorily match the size of the experimental one.

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[16] Judging from the relative intensities of the three spectra in Figure S2 of Ref. [1], it seems that the labels „293 K“ and „330 K“ have accidentally been exchanged. Otherwise, the signal intensities would have increased with increasing temperature. In addition, there are obviously inconsistencies in the scaling of the spectra.

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[18] Other compounds might contribute to the 430 nm absorption in Figure 1 b of Ref. [1]. For instance, aminyl radical **2**, which has been reported to have a pink color, absorbs weakly at 410 nm,[20] in accord with TDDFT data (Figure S2). From the data of Figure 1 b of Ref. [1], the maximum percentage of $TBA^{\bullet +}$ is roughly estimated to about 20 %, *assuming* that the 430 nm band is entirely due to $TBA^{\bullet +}$ and that the UV/Vis measurements have been performed in standard 1 cm cuvettes (no details given).

[19] Since the ESR and UV/Vis spectra indicate a low concentration of radical species, the presence of nonradical decomposition products, for example, 2,4,6-tri-*tert*-butylanilinium cation ($TBAH^+$) or hydrazine **3**, could have easily been established by ^1H NMR spectrometry.

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[23] Although it is difficult to distinguish by elemental analysis between compounds of molecular weight around 500 that differ by just one hydrogen atom, it should be noted that the C,H percentages given for the green compound (Ref. [1], p. 11881: found C 43.42, H 6.46) are closer to those for $TBAH^+$ SbF_6^- (calcd C 43.39, H 6.47) than to those for $TBA^{\bullet +}$ SbF_6^- (calcd C 43.48, H 6.28).

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