Aniline Radical Cation

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Reply to Comments on „Synthesis, Characterization, and Structures of Persistent Aniline Radical Cation“**

Xiaoyu Chen, Xingyong Wang, Yunxia Sui, Yizhi Li, Jing Ma, Jinglin Zuo und Xinping Wang**

anilines · crystal structure elucidation · EPR spectroscopy · radical cations · UV/Vis spectroscopy

We acknowledge the comments of Korth[2] and Rathore et al.[3] on our recent publication „Synthesis, Characterization, and Structures of Persistent Aniline Radical Cation“[1] and respond to the issues they raised: They criticize the characterization and structure determination of the aniline radical cation TBA$^{\bullet+}$ (TBA = 2,4,6-tri-*tert*-butylaniline), and are suspicious of its identification and related bond length changes with temperatures.

Rathore and co-workers[3] thought we had been misled by cyclic voltammetry experiments: this is not correct. Reversible oxidation waves are just an indication of the formation of radical cations but do not warrant prolonged stability. We thus stated in our paper:[1] „Cyclic voltammetry of TBA in CH_2Cl_2 at room temperature with 0.1 M Bu_4NPF_6 as a supporting electrolyte showed repeated well-defined reversible oxidation waves at $E_{1/2} = +0.78$ V versus Ag/Ag$^+$ (Figure S1, Supporting Information (SI)), indicating that the radical cation TBA$^{\bullet+}$ is stable *under these conditions*“ (italics added). This only means that radical cation TBA$^{\bullet+}$ could form at the electrochemical time scale.

Rathore et al. have obtained better absorption spectra (Figure 2B in Ref. [3]), which we recently reproduced independently. The very weak peak around 730 nm in the absorption spectrum previously was ignored by us. TBA$^{\bullet+}$ radical cation solution did slowly decompose but the radical cation still existed as its absorption peaks, typically the peak around 730 nm, were clearly observed even after 24 h. Figure 1 shows spectra reconstructed by superimposing the spectra displayed in Refs. [2,3], which include the absorption spectrum (shown as a gray line) of aliquots of the green reaction mixture (i.e. TBA + $AgSbF_6$ in CH_2Cl_2), the experimental spectrum in acetonitrile (purple line),[4] TD-UPBE0/6-31G(d)-computed excitation energies (on the UB3LYP/CBSB7-optimized geometry, green line), and TD-UPBE0/6-31G(d)-computed excitation energies of aminyl radical TBA(−H)$^{\bullet}$ (on UB3LYP/CBSB7-optimized geometries, red line). Clearly the absorption spectrum of the green solution in CH_2Cl_2 is consistent with the experimental UV spectrum in CH_3CN, and is supported by the TD-DFT calculation, but the spectrum differs from that for TBA(−H)$^{\bullet}$. The UV/Vis spectra thus strongly support the formation of TBA$^{\bullet+}$ but not TBA(−H)$^{\bullet}$.

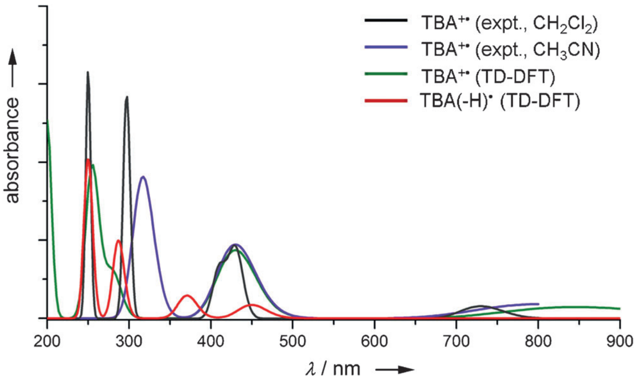

Figure 1. Absorption spectra of TBA$^{\bullet+}$ and neutral aminyl radical TBA(−H)$^{\bullet}$. The spectra were reconstructed by digitizing the spectra displayed in Refs. [2,3].

In fact we were prompted to isolate crystals of TBA$^{\bullet+}$ by its EPR spectrum, which strongly supported the formation and stability of the TBA$^{\bullet+}$ radical cation. Figure 2 shows simulated (Figure 2a) and experimental (Figure 2b) EPR spectra for TBA$^{\bullet+}$.[5] For comparison, we also added the simulated spectrum for neutral radical TBA(−H)$^{\bullet}$ (Figure 2c), using reported hyperfine coupling constants.[6] All spectra were reproduced at the same magnetic field scales. Without a doubt, the experimental EPR spectrum for TBA$^{\bullet+}$ is in good agreement with simulated EPR spectrum, but does not fit for TBA(−H)$^{\bullet}$. Note that the EPR sample was prepared by redissolving the green solid in the solvent, which

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[*] X. Chen, Y. Sui, Prof. Y. Li, Prof. J. Zuo, Prof. X. Wang
State Key Laboratory of Coordination Chemistry
School of Chemistry and Chemical Engineering
Nanjing University
Nanjing 210093 (China)
E-Mail: xpwang@nju.edu.cn

Dr. X. Wang, Prof. J. Ma
Theoretical and Computational Chemistry Institute
School of Chemistry and Chemical Engineering
Nanjing University
Nanjing 210093 (China)
E-Mail: majing@nju.edu.cn

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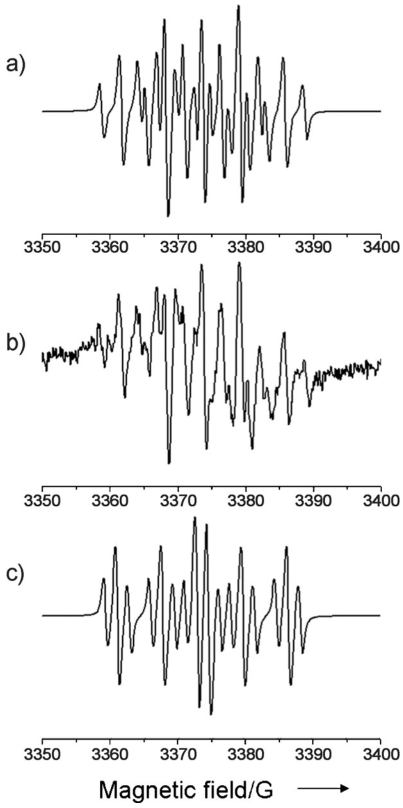

Figure 2. a) Simulated EPR spectrum for TBA$^{\bullet+}$; b) Experimental EPR spectrum for TBA$^{+\bullet}$; and c) simulated EPR spectrum for TBA(−H)$^{\bullet}$ with hyperfine coupling constants taken from Ref. [6].

together with solid-state EPR spectrum indicates that TBA$^{\bullet+}$ is also stable in the solid state. The reason why the hyperfine coupling constants given here differ from those previously reported for TBA$^{\bullet+}$ is very possibly related to a counterion effect.

Two experimental observations should not be ignored, though they are only empirical. One is, as we described as a footnote in our paper, that we found that reaction solutions of TBA with $AgSO_3CF_3$ or $AgBF_4$ rapidly turned colorless in a few minutes, while those with $AgSbF_6$ or $Ag[Al(OC(CF_3)_3)_4]$ remained green for a long time, indicating that the stability of TBA$^{\bullet+}$ is quite dependent on the anion. It is hard to believe a neutral radical species would rely heavily on the coordinating property of anions. The other observation is from thermogravimetric analysis (TGA). We observed no color and weight change when crystals were heated to 100 °C under N_2 for more than three hours, suggesting that the crystal is stable at the X-ray diffraction time scale.

In our crystallographic experiments, although the bond lengths in the aromatic ring show alterations with temperature, these changes are not significant from 123 K to 273 K if large errors are considered. As we stressed in the text, however, bond length changes are significant between the two structures determined at 123 K and 373 K. We do not understand why Rathore et al. did not determine X-ray structures for the green crystal at room temperature or above, since they already had crystals at hand. They claim that hydrogen atoms were directly found in the difference map, but those Q peaks might not be real atoms.[7] The structure shown in Figure 1 in Ref. [3] does not show F⋯H distances. They also claim they have the same unit cell for the colorless crystals, which unfortunately had been ignored by us. However, it could be coincident that green and colorless crystals have similar unit cell parameters. The two structures should be comparably studied in detail but not just unit cell parameters.

In order to check the disorder in TBA$^{\bullet+}$ crystal structures, we repeated reactions of TBA and $AgSbF_6$ (molar ratio = 1:1) several times and green products were crystallized at various temperatures (−30, −20 °C, etc.). After careful determination of X-ray diffraction crystal structures at −123 K, we found that the TBA$^{\bullet+}$ salts that crystallized at different temperatures show various degrees of twinning (Figure 3).[8] We also found that disorder of structures is more or less related to the degree of twinning and affects bond length of phenyl rings.[9] On the other hand, based on the comments by Korth and Rathore et al., together with our own work, it is also possible that TBA$^{\bullet+}$ cocrystallized with TBAH^{+}, which resulted in crystals with different properties which presented difficulties in the structure determination.

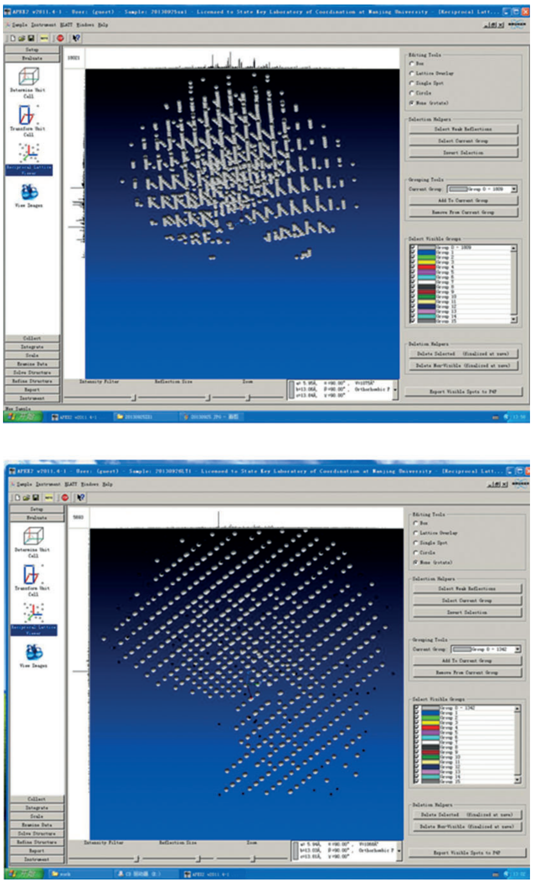

Figure 3. View of the reciprocal lattice of TBA$^{\bullet+}$ crystals. Top: heavily twinned crystals; bottom: slightly twinned crystals.

It is true that the spin contamination of UMP2 calculations is large compared to that of DFT methods. Hence, the latter are usually applied to describe the electronic structure of open-shell systems. DFT methods are able to predict strong covalent bonding pretty well, but they are unsuitable for accurately describing weak interactions (e.g. hydrogen bonding, dispersion forces, and π–π interactions), although some DFT methods have been improved in energy calculation for weak interactions.

The orbital energy levels for TBA$^{\bullet+}$ („bisallyl, 123 K“ X-ray structure, as in Figure S2 A in the Supporting Information of Ref. [3]) are shown in Figure 4. According to the energy level order, we presented only α-SOMO and α-HOMO-1 orbitals without showing the corresponding β orbitals. Without looking into all the occupied α and β orbitals, how can we conceive of the perfect matching of α and β orbitals and neglect the open-shell character of TBA$^{\bullet+}$? We did not mention that α-SOMO corresponds to the wavefunction of the unpaired electron, and to the spin density distribution in TBA$^{\bullet+}$. It is worth noting that β-HOMO is not totally identical to α-SOMO. Since spin density is the total electron density of α-spin electrons minus that of β-spin electrons, $\rho^S(\mathbf{r}) = \rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r}) = \sum^{N^\alpha} \left|\Psi^\alpha_a(\mathbf{r})\right|^2 - \sum^{N^\beta} \left|\Psi^\beta_a(\mathbf{r})\right|^2$, it is not appropriate to conclude that the „α-SOMO does not contribute to the spin density“ just based on the appearance that the „β-counterpart of α-SOMO is an occupied orbital“ (quotations from the Supporting Information of Ref. [3]).

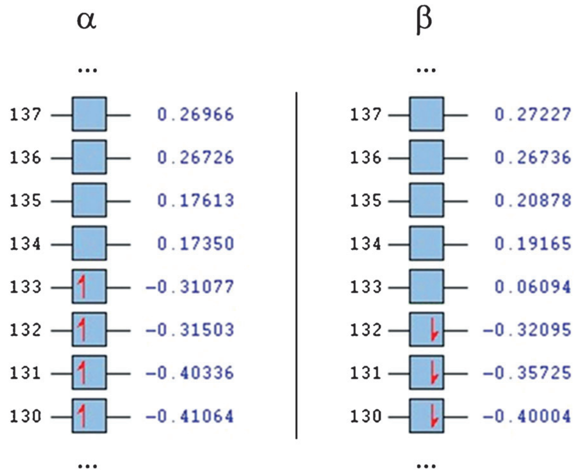

Figure 4. The energy levels for TBA$^{\bullet+}$ („bisallyl, 123 K“ X-ray structure).

We agree with Korth's point that „a JT distortion must be expected for a high-symmetry structure having a (nearly) degenerate ground state“. In fact, we did not claim in our text that the presence of two isomers for TBA$^{\bullet+}$ is ascribed to the Jahn–Teller effect, but the citation of JT distortion for benzene radical cation may be somewhat misleading.

In conclusion, UV/Vis absorption and EPR spectra have unambiguously demonstrated that TBA$^{\bullet+}$ is persistent and stable. However, its crystal structures appear more complicated than we expected. In order to make a thorough clarification and gain complete understanding, further investigations are needed. This includes more recollections of X-ray diffraction data on both green and colorless crystals, varible-temperature FT Raman/IR measurements to check bond length changes,[10] and more reactions using larger and weakly coordinating anions. These investigations are underway and the results will be reported in due course. Finally we thank Korth[2] and Rathore et al.[3] again for their comments, which push us to further study and clarify this issue.

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[1] X. Chen, X. Wang, Y. Sui, Y. Li, J. Ma, J. Zuo, X. Wang, *Angew. Chem.* **2012**, *124*, 12048 – 12051; *Angew. Chem. Int. Ed.* **2012**, *51*, 11878 – 11881.

[2] H.-G Korth, *Angew. Chem.*, DOI: 10.1002/ange.201303991; *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.201303991.

[3] M. R. Talipov, J. S. Hewage, S. V. Lindeman, J. R. Gardinier, R. Rathore, *Angew. Chem.*, DOI: 10.1002/ange.201305293; *Angew. Chem. Int. Ed.* DOI: 10.1002/anie.2015293.

[4] B. Speiser, A. Rieker, S. Pons, *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *147*, 205 – 222; B. Speiser, A. Rieker, S. Pons, *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *159*, 63 – 88.

[5] The solvent should be CH_3CN and the concentration is in the range of 10^{-3}–10^{-2} $mol\,L^{-1}$. We thank H.-G. Korth for pointing out this issue.

[6] G. Cauquis, M. Genies, *C. R. Hebd. Seances Acad. Sci. Ser. C* **1967**, *265*, 1340 – 1343.

[7] Instead neutron diffraction method may be reliable.

[8] Cell parameters for a) heavily twinned crystal: orthorhombic, $a = 5.95$, $b = 13.06$, $c = 13.84$ Å, $V = 1075$ Å^3; and b) lightly twinned crystal: orthorhombic, $a = 5.94$, $b = 13.03$, $c = 13.81$ Å, $V = 1068$ Å^3.

[9] We found that the structure of $TBA^{\bullet+}SbF_6^-$ in the heavily twinned crystal is relatively ordered.

[10] We thank Prof. Ingo Krossing for his suggestions on the use of variable-temperature FT Raman/IR for checking bond length changes and NH_2/NH_3 vibration modes.