ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2023, **59**, 595

Received 3rd October 2022,
Accepted 13th December 2022

DOI: 10.1039/d2cc05404c

rsc.li/chemcomm

An air-stable radical with a redox-chameleonic amide†

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An air-stable (amino)(amido)radical was synthesized by reacting a cyclic (alkyl)(amino)carbene with carbazoyl chloride, followed by one-electron reduction. We show that an adjacent radical center weakens the amide bond. It enables the amino group to act as a strong acceptor under steric contraint, thus enhancing the stabilizing capto-dative effect.

Glycyl radical enzymes are important biocatalysts that enable a variety of transformations; from the reduction of nucleotides to the breakdown of inactivated hydrocarbons.[1] Their active resting state is generated by H atom abstraction at a glycine residue (Fig. 1a). The resulting C-radical **A** is highly sensitive to oxygen and the enzymatic processes work only under anaerobic conditions. Note that other reactive peptidyl radicals and related (amino)(amido) C-radicals **B** are rare in nature,[1c,d] but are commonly involved in synthetic radical peptidic chemistry.[2]

The persistence of the glycyl C-radical pattern in enzymes is usually attributed to the synergic combination of an electron-donating nitrogen (blue on Fig. 1) and an electron-withdrawing carbonyl group (red), a push-pull or captodative effect.[3] The protein environment also precludes the formation of C–C dimers, which are usually obtained with simpler molecular models.[3e–i] In 2013, we took advantage of the bulky pattern of cyclic (alkyl)(amino)carbene (CAAC)[4–6] to synthesize and isolate monomeric (amino)(carboxy) C-radical **C** under inert atmosphere.[5a] In addition, we showed that increasing the electron-withdrawing properties of the carbonyl substituent, such as in compound **D**, resulted in radicals with remarkable air-persistency.[5d,7] A schematic molecular orbital analysis enables the rationalization of this effect. Indeed, the singly occupied molecular orbital (SOMO) is a bonding combination of π^*_{CO} and π^*_{CN} (Fig. 1b). An electron-withdrawing substituent on the carbonyl lowers the energy of the π^*_{CO}, thus increasing the weight of the CO fragment, which has major coefficient on oxygen. Therefore, the formal C-radical shifts to more of an O-centred radical, which is less reactive towards dioxygen.[5d,8]

In this context, as illustrated by the high air-sensitivity of glycyl radical enzymes, amide patterns seem especially unfit for the design of bench-stable radicals; they are among both the poorest available N-donors and the weakest electron-withdrawing carbonyl groups. Herein, we challenge this paradigm and report an air-stable version of an amide-substituted

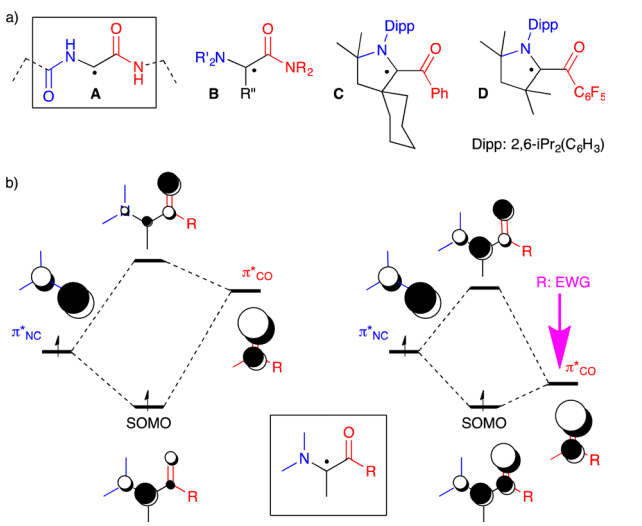

Fig. 1 (a) Glycyl radical pattern **A** in Enzymes, (amino)(amido) C-radical **B**, bottle-able push-pull C-radical **C** (air sensitive) and **D** (highly air-persistent); (b) schematic representations of SOMO of an (amino)(carbonyl) C-radical built from π^*_{NC} and π^*_{CO}, left: "classical" case, right: R is an extreme electron-withdrawing group.

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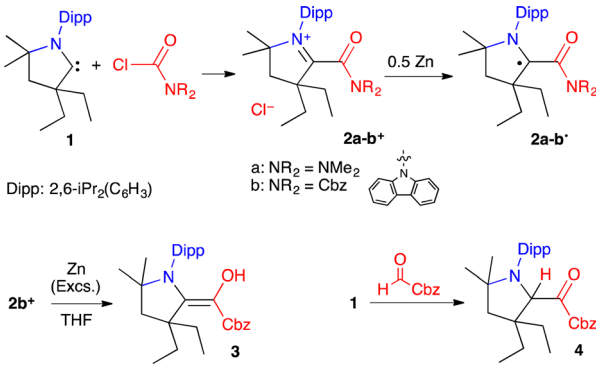
† Electronic supplementary information (ESI) available: Experimental procedures, analytical and computational data. CCDC 2191398 and 2191542–2191545. For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d2cc05404c



Scheme 1 Synthesis of radicals **2a-b•** and their derivatives.

captodative radical. We show that the adjacent radical centre weakens the amide bond and enables the N-group to act as a strong acceptor.

We initially considered a simple *N*,*N*′-dimethylamido group. The chloride salt of acylium **2a**$^+$ was synthesized by the addition of CAAC **1** to dimethylcarbamoyl chloride (Scheme 1). Cyclic voltammetry indicated two reversible reductions at −1.34 and −2.00 V (*versus* Fc/Fc$^+$), corresponding to the formation of **2a•** and the enolate **2a**$^-$, respectively (Fig. 2a). Radical **2a•** was generated *in situ* by bulk electrolysis at −1.43 V. This highly air-sensitive radical was also synthesized by chemical reduction of acylium **2a**$^+$ with 0.5 equivalent of Zn(0) and isolated as a yellow solid in 88% yield. A single crystal X-ray diffraction study (Fig. 2b) revealed a dimethyl amino group with pronounced pyramidalization (sum of angles around N2: 331.6°). The lone pair of the amide nitrogen is not conjugated, but perpendicular to the carbonyl. As a result, the long C2–N2 distance (143.7 pm) is typical for a single bond and sharply contrasts with the usual bond length in planar acyclic amides (132–134 pm).[9]

Acyclic twisted amide patterns usually require the deactivation of the nitrogen with an ancillary electron-withdrawing substituent or the incorporation into an aromatic ring.[10,11] The local environment of N2 is more reminiscent of "anti-Bredt" amides or ureas, which feature a polycyclic saturated backbone with a bridgehead nitrogen.[12,13] These compounds are not stable when there is a significant twisting around the (OC)–N bond, as they feature both an activated electrophilic carbonyl and a nucleophilic nitrogen centre. In radical **2a•**, the twist of the *N*,*N*′-di(methyl)amino group is maximal; however the amine acts as a strong electron-withdrawing group, which is a favourable electronic situation for a push-pull radical.[5]

We turned to a carbazole substituent to increase the electron-withdrawing capability of the carbonyl moiety. We synthesized acylium **2b**$^+$ (Scheme 1). Cyclic voltammetry featured two reversible processes at −0.63 and −1.59 V, which are significantly more positive values than in the case of **2a**$^+$ (Fig. 2). Radical **2b•** was generated *in situ* by bulk electrolysis at −0.78 V. The radical was also synthesized by chemical reduction of acylium **2b**$^+$ with 0.5 equivalent of Zn(0) and isolated as a colourless solid in 84% yield. Of note, attempts to further reduce the radical with one equivalent of Zn(0) lead

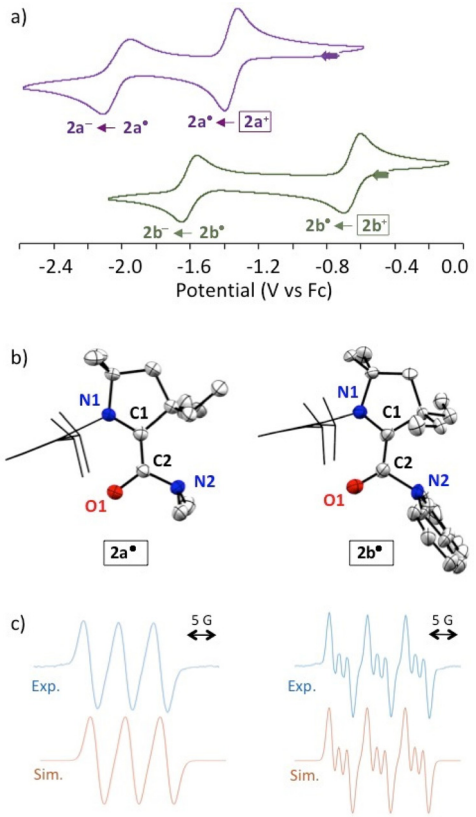


Fig. 2 (a) Cyclic voltammograms of a 1 mM solution for both the chloride salt of **2a**$^+$ (top) and **2b**$^+$ (below) in 0.1 M ^{n}Bu$_4$NPF$_6$ acetonitrile solution at 100 mV s^{-1} rates. (b) Solid state structures of radicals **2a•** and **2b•**. Thermal ellipsoids are set to 50% probability. Molecules of solvent, hydrogen atoms and ellipsoids on 2,6-diisopropylphenyl groups are omitted for clarity. (c) top: X-band EPR spectra of **2a•** (left) and **2b•** (right) in acetonitrile at room temperature; below: corresponding simulated spectra with the following set of parameters: **2a•**, Lorentzian line-broadening parameter L_w = 0.264 and hyperfine coupling constant a(^{14}N) = 15.8 MHz (1 nucleus); **2b•**, L_w = 0.143, a(^{14}N) = 18.3 MHz (1 nucleus) and 4.0 MHz (1 nucleus).

after work-up to the isolation of few crystals of the corresponding enaminol **3** (Scheme 1), which was characterized by X-ray diffraction (see ESI†). As in **2b•**, the carbazole is orthogonal to the carbonyl. This is in line with a previous study by Berkessel *et al.*, which shows that strong electron-withdrawing groups stabilize Breslow-type enols.[14] Interestingly, we were also able to isolate the corresponding keto tautomer **4** from the reaction of CAAC with *N*-formyl carbazole.[15]

As for **2a•**, a single crystal X-ray diffraction study of **2b•** revealed a pyramidalized N2 centre (sum of angles around N2: 330.7°), a formal lone pair perpendicular to the carbonyl and a long C2–N2 distance (143.3 pm).[16] Importantly, in marked contrast with sensitive radical **2a•**, **2b•** is remarkably robust towards air in the solid state and in toluene. The observation of a fast decay by EPR monitoring required heating an aerated solution in ethanol at 60 °C.

DFT[17] optimized structures of **2a-b•** at the b3lyp/6-311g(d,p) level of theory matched the experimental solid-state geometries, as well as the EPR isotropic hyperfine coupling constants,[18]

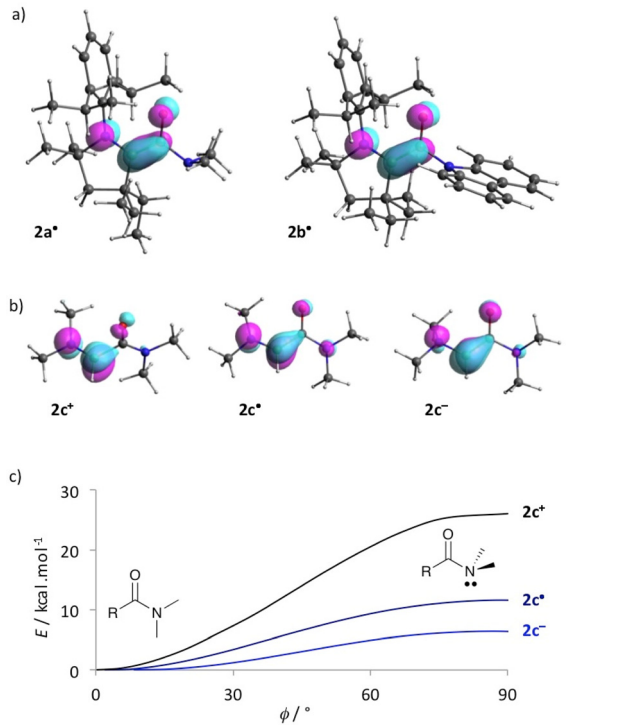


Fig. 3 (a) Optimized DFT geometry of **2a-b•** with representations of corresponding SOMO. (b) Optimized DFT geometry of model **2c⁺**, **2c•** and **2c⁻** with representation of corresponding LUMO, SOMO and HOMO, respectively. (c) Energy in relaxed scan optimization of **2c⁺**, **2c•** and **2c⁻** as a function of ϕ, the torsion angle between the formal N lone pair and the π_{CO} molecular orbital.

(Fig. 2c; **2a•**, computed $a(^{14}N)$: 14 MHz, experimental: 15.8 MHz; **2b•**, computed $a(^{14}N)$: 16 and 3 MHz, experimental: 18.3 and 4.0 MHz). The distribution of the Mulliken spin density (see also the representation of SOMO in Fig. 3a) is similar for both radicals (**2a•**: N1: 25%, C1: 41%, C2: 7%, O1: 26%; **2b•**: N1: 25%, C1: 37%, C2: 7%, O1: 30%). These values are reminiscent of the spin distribution of highly air persistent radical **D**, featuring a perfluorophenyl in place of the twisted amino groups. This suggests that the O-centred character of **2a-b•** was sufficient to disfavour triplet oxygen addition at the C1 atom.[5d,8] Accordingly, this reaction is predicted to be endergonic for **2a-b•** by ΔG = +10.2 and +21.2 kcal mol^{-1}, respectively. Thus, we considered that a single electron transfer to dioxygen was a more plausible initiation step for the pathway of decay of **2a•** in the presence of air. Indeed, radical **2a•** stands out with a very low oxidation potential (−1.34 V) when compared to previously reported CAAC-based (amino)(carboxy)radicals (from −0.2 V to −0.9 V).[5] Note that the computed ionization potential fits well with values for parented radicals (**2a•**: 5.1, **2b•**: 5.4, **C**: 5.1 and **D**: 5.5 eV). However, the conformational relaxation of **2a⁺**, which follows the vertical ionization of **2a•**, is especially exothermic (**2a**: −28, **2b**: −19, **C**: −19 and **D**: −15 kcal mol^{-1}). Therefore, we concluded that the low oxidation potential of **2a•** was also due to the singular stability of **2a⁺** compared to other acyliums of the series. Indeed, the di(methyl)amino group has a chameleonic behaviour: it is twisted and acts as a −I attractor in radical **2a•**, but it is a fully conjugated strong +M donor (stronger than the aromatic carbazole of **2b⁺**) in acylium **2a⁺**.

To get further insights, we considered simplified acylium, radical and enolate, **2c⁺**, **2c•** and **2c⁻** respectively, which feature a dimethylaminocarbene in place of the bulky CAAC pattern. Note that in acyliums **2a–c⁺** the iminium moieties are perpendicular to the carbonyl, whereas the N–C–CO pattern is fully conjugated in radicals **2a–c•** and enolates **2a–c⁻**. Interestingly, the small model compound **2c•** differs from CAAC-based radicals **2a–b•** with a fully conjugated amide moiety and only a slight pyramidalization at the nitrogen is found in **2c⁻**; the conformations of **2c⁺**, **2c•** and **2c⁻** with formal N2 nitrogen lone pair perpendicular to the carbonyl are transition states (Fig. 3b). However, introducing a radical or an anion in α position of the carbonyl significantly weakens the amide bond. Indeed, the formal one electron reduction to afford **2c•** (respectively **2c⁻**) consists in populating the LUMO of **2c⁺** (SOMO of **2c•**, respectively) with anti-bonding character between C2 and N2. Accordingly, the energy barrier for full twisting dramatically decreases from **2c⁺** ($\Delta G^{\neq}$ = +26.2 kcal mol^{-1}) to **2c•** (+7.1 kcal mol^{-1}) and **2c⁻** (+6.7 kcal mol^{-1}).

Amido groups have been classified as latent rotational stereoelectronic chameleons by Alabugin *et al.*[19] Misalignment of the nitrogen lone pair with the carbonyl usually requires polycyclic structures or high steric strain; however, the enhanced flexibility of an amide bond that results from an adjacent radical centre has gone unnoticed to date. Beyond implications for the design of bench-stable organic radicals, it is likely that natural evolution has already taken advantage of such redox-chameleonic behaviour.[20] This effect should not be overlooked in future studies on glycyl enzymes or peptidyl radical chemistry.

This work was supported by the French-American cultural ex-change foundation (FACE), the NSF (CHE-1954380) and the French National Agency for Research (ANR-14-CE06-0013-01 and CBH-EUR-GS, ANR-17-EURE-0003). Thanks are due to the CECCIC and the ICMG platforms of Grenoble.

Conflicts of interest

There are no conflicts to declare.

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