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A Potent Auto-Umpolung Ligand for Conjugative Radical Stabilization

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Abstract: Carbenes with conjugatively connected redox system act as "auto-umpolung" ligands. Due to their electronic flexibility, they should also be particularly suitable to stabilize open-shell species. Herein, the first neutral radical of such sort is described in form of a dialkylamino-substituted bis(dicyanomethylene)cyclopropanide. Despite the absence of steric shielding, the radical is stable for an extended amount of time and was consequently characterized in solution via EPR measurements. These data and accompanying X-ray structural analyses indicate that the radical species is in equilibrium with aggregates (formed via π-stacking) and dimers (obtained via σ-bond formation between methylene carbons).

Introduction

In previous work, we have identified a class of ligands **1** with chameleonic properties (Figure 1, top).[1] Here, a two-step redox system (RED/OX) is conjugatively connected with a trigonal carbon center, which can be attached to various substrates via its free valence. To which extent resonance structures **A** or **B** dominate in the "redox resonance" of **1** depends on the electronic structure of the appended substrate. If the latter is a donor moiety, **A** will prevail, if it is an acceptor moiety, **B** will be the major contribution. Systems featuring this electronic flexibility have been termed "auto-umpolung"[1e] ligands (see examples **1 a**–**e** in Figure 1, bottom).[2]

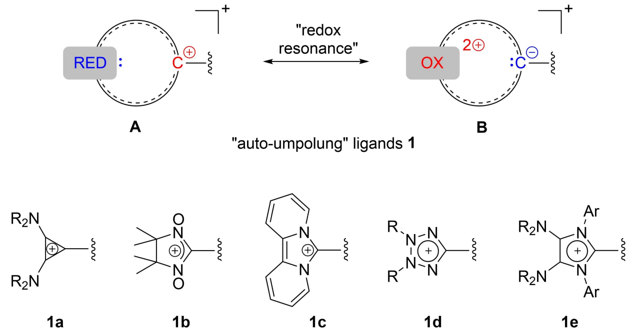

Figure 1. Top: Schematic depiction of "auto-umpolung"; RED/OX = reduced/oxidized form of redox system. Bottom: Previous examples of "auto-umpolung" ligands; R = alkyl, Ar = aryl; anions omitted.

As such π-systems are capable of stabilizing both donor and acceptor centers on demand, they are then *a fortiori* also predestined to stabilize radical centers (which are known to profit from interactions with both types of substituents). Examples for this approach exist in the literature, although the general principle has not yet been fully recognized.

This refers most prominently to bis(dimethylamino)cyclopropenium salts, i.e. derivatives of **1 a**.[1a,b,c,3] The corresponding aminiumyl radical (with NMe_2 as third substituent) was the first stable dication radical salt, generated by Gerson in 1971[4] and isolated by Weiss in 1975.[5] More recently, the groups of Sanford and Lambert succeeded to crystallize dicationic radicals based on this trisaminocyclopropenium (TAC) scaffold[6,7] and tested their stability towards air and water.[7] Due to the high persistency of their radicals, TAC salts and their derivatives are used as redoxactive polymers,[8] as catholytes in all-organic redox flow batteries,[7,9] as redox shuttles to prevent overcharge in Na batteries,[10] and as electrophotocatalysts for the coupling of benzene and halogenated benzenes with azoles.[6] Lately, further derivatives of **1 a**, featuring an oxo or a thioether substituent, have been successfully oxidized to the respective radical.[9,11]

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All auto-umpolung ligands **1 a**–**1 e** (Figure 1) are positively charged, but other charge types are also feasible. In 1976, Fukunaga introduced the dicyanomethid-substituted cyclopropenium dianion **2** (Figure 2),[12] which can be oxidized to a persistent monoanionic radical **2'**.[13]

We reasoned that the corresponding ligand **3** (Figure 2, red) should also constitute a powerful auto-umpolung system capable of strong radical stabilization. However, even though some monoanionic derivatives of scaffold **3** were reported by the groups of Fukunaga and Seitz,[12,14] their ability to form persistent radicals was not extensively studied.

All reported radicals based on ligands **1 a**–**1 e** are either cationic or anionic. Herein, we report the synthesis and properties of an aminiumyl radical based on ligand **3**, which constitutes the first *neutral* radical of this sort. Its relative stability (which is *not* influenced by steric or electronic effects of counterions) and further computational studies demonstrate that ligand **3** is markedly superior to classical systems like **1 a** in terms of radical stabilization.

Results and Discussion

First, DFT calculations (M06-2X[15] def2-TZVP[16]) on the isodesmic reaction shown in Scheme 1[17] were performed to quantify the (carbon) radical stabilization induced by ligand **3** in comparison to classical donor/acceptor substituents or other cyclopropenium ligands.[18]

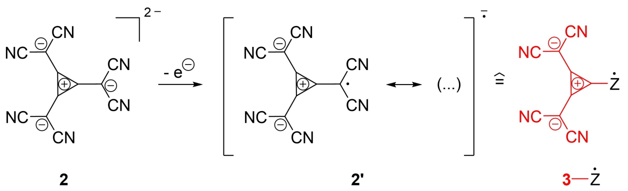
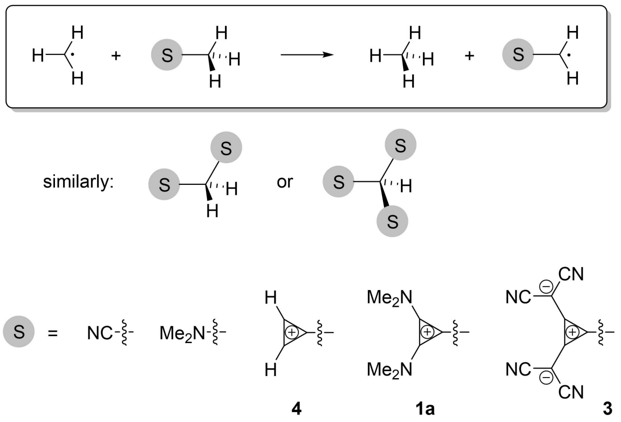


Figure 2. Fukunaga's dianion **2**, its corresponding radical anion salt **2'** and ligand **3** (cations omitted; Z = substituent, here -C(CN)$_2$). Cations omitted for clarity.



Scheme 1. Isodesmic reaction to evaluate radical stabilisation (see also Table 1).

The results (Table 1) indicate that ligand **1 a** (entry 5) is about as stabilizing as one amino substituent (entry 4), while ligand **3** (entry 8) is markedly outperforming *two* donor (entry 6) or *two* acceptor (entry 7) substituents and reaches almost the stabilization induced by a capto-dative setup (entry 9). This is very remarkable, as **3** is thus able to exert capto-dative-like stabilization but with just one ligand. In contrast to the capto-dative setup, however, ligand **3** can be attached multiple times to the same radical center (entries 10 and 11) to amplify its effect.

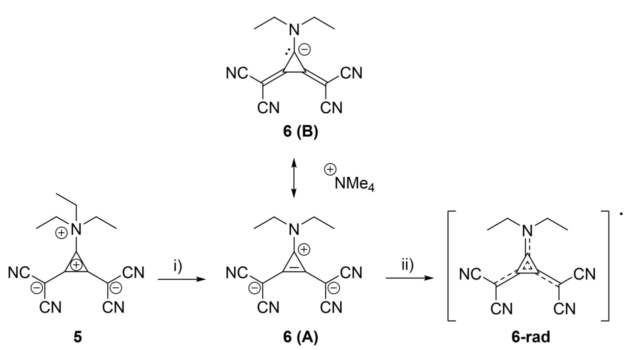
The superior stabilizing capabilities of **3** compared to **1 a** may be due to a higher-energy HOMO and a smaller HOMO-LUMO gap (7.1 eV for **3** vs. 8.7 eV for **1 a**). The spin densities on the formal radical center (Table 1) also show the most pronounced delocalization for ligand **3**.

As experimental system to study radical stabilization, we opted for amino-substituted precursor **6** (Scheme 2), as we had seen in other context[19] that it can be obtained by dealkylation of known salt **5** with iodide. A planarized amino nitrogen in the solid-state structure of **6** (see Supporting Information) confirms the expected predominance of resonance structure **6** (**A**) (Scheme 2). Fittingly, its ^{13}C NMR spectrum indicates slow rotation around the C_3–$C(CN)_2$ bond (see Figure S10 in Supporting Information). In precursor **5**, however, two well-separated signals for the cyano groups corroborate **B**-type umpolung.

Table 1. Calculated[a] gas-phase enthalpy (ΔH) and Gibbs free energy[b] (ΔG) for the isodesmic reactions of Scheme 1 (all in kcal mol^{-1}) and Mulliken spin density at the "spin-bearing" carbon atom (in %).

	S–H	ΔH	ΔG	spin density
1	H	0	0	91
2	CN	−8.1	−7.2	59
3	**4**	−9.1	−7.7	71
4	NMe$_2$	−12.4	−12.0	71
5	**1 a**	−13.9	−12.1	46
6	2x NMe$_2$	−13.2	−13.1	70
7	2x CN	−16.1	−15.2	44
8	**3**	−21.7	−19.6	26
9	CN and NMe$_2$	−24.7	−24.6	42
10	2x **3**	−33.4	−31.3	19
11	3x **3**	−42.1	−39.8	18

[a] M06-2X/def2-TZVP [b] including low frequency entropy correction.



Scheme 2. Dealkylation reaction of **5** to obtain radical precursor **6** and subsequent oxidation to radical **6-rad**. i) tetramethylammonium iodide, MeCN/H$_2$O, 70 °C, 12 h, 62 %; ii) 0.5 eq bromine, DCM, r.t.

Electrochemical measurements on precursor **6** (see Figure 3, red) demonstrate its chemically reversible oxidation with $E_m = +0.20$ V vs. Fc/Fc$^+$ (a shift of $+0.21$ V compared to dianion **2**).[20] A second, chemically irreversible oxidation (at a scan rate of 100 mV s^{-1}) was detected at $E_{ox} = +1.10$ V vs. Fc/Fc$^+$.

Both SOMO and spin density plots of presumably created neutral radical **6-rad** display broad spin distribution over the whole molecule (see Supporting Information). Except for the ethyl groups, the compound is entirely flat. Thus, due to the absence of steric shielding (and counterions), any persistency of the radical species can be purely attributed to electronic factors.

Elemental bromine should be sufficient to oxidize **6**, and indeed after addition of the halogen to a solution of the latter in organic solvents, the colourless solution turned intensely green. A reversible redox process was once again detected for the product obtained after aqueous work-up (Figure 3, black), albeit with a mid-point potential of -0.02 V vs. Fc/Fc$^+$. It is currently unclear which effect (e.g. electrolyte composition, aggregation) is responsible for the difference in potentials.[21] The chemical oxidation is also reversible, as the green colour vanishes upon treatment with $Na_2S_2O_3$ but can be revived with further bromine.

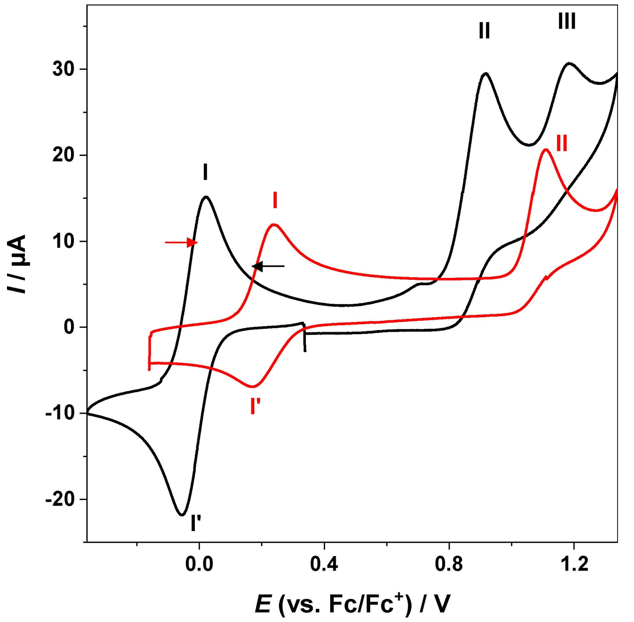


Figure 3. Cyclic voltammogram (in 0.1 M NBu_4PF_6/MeCN at a glassy carbon electrode) for **6-rad**, starting from precursor **5** (red) and generated by treatment of **5** with Br_2 (black) (scan rates of $v = 100$ mV s^{-1}).

In orientating UV-vis measurements to investigate radical stability, apparently different degradation processes were observed depending on the overall concentration (see Supporting Information). In one case, no changes were detected within eight days, demonstrating the pronounced persistency of **6-rad** even without exclusion of air and moisture.

EPR measurements further elucidated the nature of the radical species. At room temperature, in predominantly aqueous solution (MeCN:water = 8:92, 0.5 mM concentration) a defined hyperfine-coupled spectrum was obtained (Figure 4a, black). The simulated spectrum of radical **6-rad** featuring a complex signal pattern due to $^{14}N/^{1}H$ spin couplings corroborated the assignment of the experimental spectrum to **rad-6** (Figure 4a, red; see Supporting Information). In organic solvents (MeCN, MeCN:H_2O = 3:1 or chloroform), however, a broad signal was observed (Figure 4b, black), even upon dilution to 0.05 mM. The broadening indicates aggregation, and indeed the simulated spectrum of a stacked dimer of **6** with **6-rad** (using the hyperfine parameters obtained by DFT) (Figure 4b, red) strongly resembles the experimental one. Interactions between two **rad-6** moieties in a triplet state were also considered, which also led to similarly broad EPR features (Figure 4c, red, see Supporting Information). Therefore, it is not possible to unveil the exact origin of the broad signal observed by room temperature analysis. In MeCN:water = 3:1 (5 mM), the signal intensity had decreased after 80 min (black, dashed) but was still observable. Radical **6-rad** thus markedly outrivals a TAC-based analogue in stability, as the latter is reduced in 15 min upon addition of only 2% water.[7] The EPR data clearly show that aggregate formation of **6-rad** is prevented in predominantly aqueous solution.

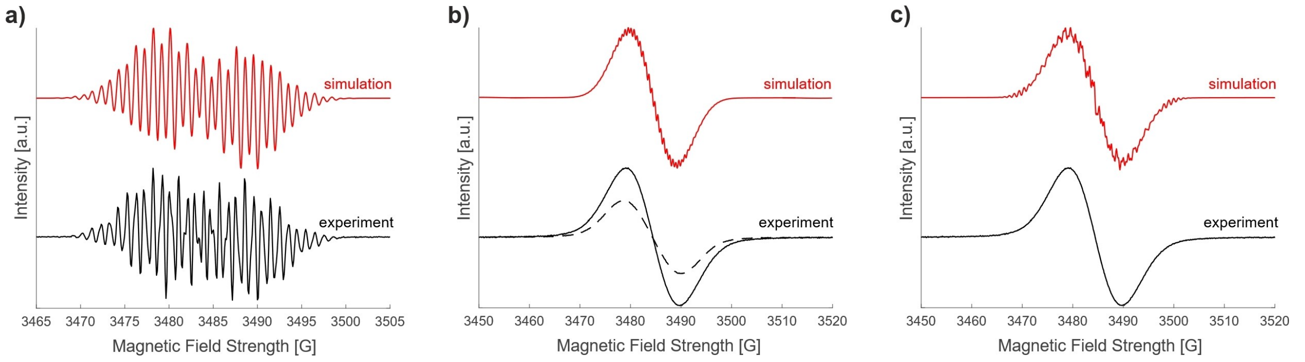


Figure 4. EPR-measurements of radical species deriving from precursor **6** (black) compared to simulated spectra in liquid state (red). a) Experimental data in MeCN:H_2O = 92:8 (0.05 mM) at room temperature (black). Simulation of free **6-rad** (doublet, red). b) 5 mM in MeCN:H_2O = 3:1, after bromine addition (solid line, black) and 80 min later (dashed, black). Simulation of dimer **6**·**6-rad** (doublet, red). c) 5 mM in MeCN:H_2O = 3:1, after bromine addition (black, as in panel b). Simulation of dimer π-[**6-rad**]$_2$ (triplet, red).

Next, the structure of **6-rad** in the solid state was analysed. In three different crystallization vessels, three different crystals were obtained from the same starting material by diffusion of diethyl ether or cyclopentane into a DCM solution. Figure 5 shows "pancake-bonding"-like[22] π-dimers of **6-rad**, found in metallic dark-bronze crystals, which feature an interacting distance of 3.08 Å. All geometric parameters – longer C–C bonds within the cyclopropenium unit (1.398 Å) and shorter ones towards the substituents (1.381 Å)–point towards a **6** (**B**)-like resonance structure as the most relevant (see Supporting Information). Other compounds like phenalenyl or tetracyanoethylene radicals also form similar π-dimers,[23] with comparable C–C distances between 2.87 and 3.32 Å.[23a,b]

Bluish-green needles consisted of co-crystals of starting material **6** and its radical form **6-rad** (denoted as [**6**·**6-rad**]$_n$), which featured infinite chains formed by stacking of the three-membered rings (for further details see Supporting Information). Lastly, dark green crystals contained σ-bonded dimers σ-[**6-rad**]$_2$ (Scheme 3, see also Supporting Information) with very long C^{sp3}–C^{sp3} single bonds (1.633 Å) between two $\underline{C}(CN)_2$ carbons. Similar bond lengths were observed for other σ-bonded radical dimers.[23c,d]

The three crystal structures illustrate that free radical **6-rad**, which was detected in aqueous solution via EPR, is in equilibrium with several other di- or polymeric aggregates (see Scheme 3). DFT calculations indicate that the formation of π-dimers/aggregates is preferred over σ-dimerization (see Supporting Information). We note that diamagnetic σ-[**6-rad**]$_2$ was not detected in solution via ^1H NMR spectroscopy. Dimer π-[**6-rad**]$_2$ can exist in singlet or triplet state (with orientating DFT calculations prefering the singlet state by few kcal mol^{-1}). The aggregates observed in EPR-measurements are consistent with [**6**·**6-rad**]$_n$ and cannot exclude triplet π-[**6-rad**]$_2$ (including higher aggregates).

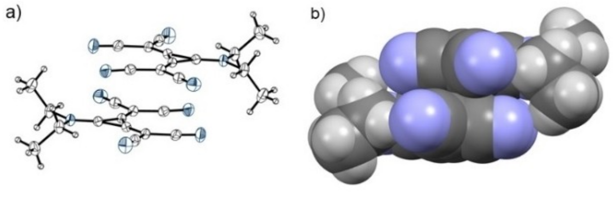
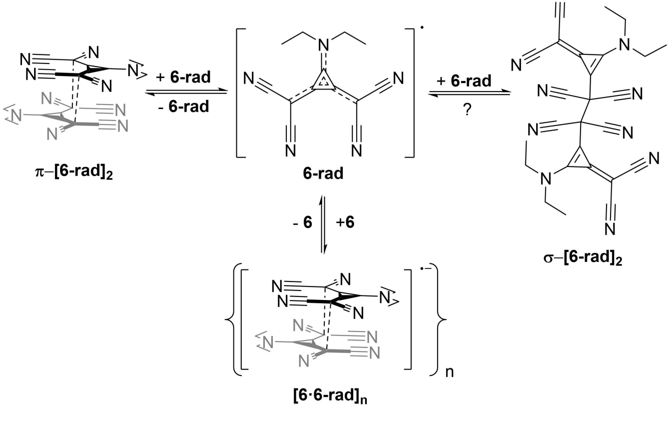


Figure 5. a) Dimer motif of radical **6-rad** (ellipsoids at 50% probability); b) space-filling model of π-[**6-rad**]$_2$.



Scheme 3. Possible equilibria of **6-rad** as indicated by X-ray analysis and EPR-spectroscopy.

Conclusion

Auto-umpolung ligands feature a high electronic flexibility which makes them also prime candidates for the stabilization of open-shell species. DFT calculations indicate that the bis(dicyanomethylen)cyclopropanide scaffold is a particularly powerful representative of this class, exerting almost the same stabilizing effect as *two* donor/acceptor substituents in a classical capto-dative setup – yet in an *ipso* fashion. Herein, the first example of a neutral radical stabilized by auto-umpolung ligands was presented in the form of **6-rad**. Even though this radical, which was identified in solution via EPR, is not sterically shielded, it is persistent and can exist in solution for at least 8 days. EPR measurements and X-ray analysis demonstrated that **6-rad** is involved in several dynamic processes involving dimerization and aggregation.

Experimental Section

Full details of all experiments and characterisation data of the described compounds are given in the Supporting Information.

1,2-Bis(dicyanomethylene)-3-triethylammonium-cyclopropanide (**5**) was prepared according to a reported procedure.[12a]

Synthesis and characterization of tetramethylammonium 1,2-bis(dicyanomethylene)-3-diethylamino-cyclopropanide (6)

Precursor **5** (0.50 g, 1.88 mmol, 1.00 eq.) was dissolved in 15 mL acetonitrile and 0.38 g (1.88 mmol, 1.00 eq.) tetramethylammonium iodide was added. To increase the salt's solubility, a few drops of water were added. The reaction mixture was stirred at 80 °C for 13 h. Afterwards, the solvent was removed under reduced pressure and the crude product was reprecipitated from DCM with diethyl ether. The obtained powder was crystallised for further purification. Therefore, it was dissolved in DCM and diethyl ether was used as co-solvent. Product **6** was obtained as a colourless powder in 62% yield (360 mg, 1.16 mmol).

M.p. 183 °C; ^1H NMR (chloroform-d_1, 300 MHz, 300 K): $\delta = 3.44$ (bs, 4H, CH_2), 3.29 (s, 12H, $N(C\underline{H}_3)_4$), 1.25 (t, $J = 7.2$ Hz, 6H, $CH_2C\underline{H}_3$) ppm; ^1H NMR (DMSO-d_6, 300 MHz, 300 K): $\delta = 3.36$ (q, $J = 7.1$ Hz, 4H, $C\underline{H}_2$), 3.10 (s, 12H, $N(C\underline{H}_3)_4$), 1.15 (t, $J = 7.1$ Hz, 6H, $CH_2C\underline{H}_3$) ppm; ^1H NMR (acetonitrile-d_3, 300 MHz, 295 K): $\delta = 3.40$ (q, $J = 7.2$ Hz, 4H, $C\underline{H}_2$), 3.07 (m, 12H, $N(C\underline{H}_3)_4$), 1.19 (t, $J = 7.2$ Hz, 6H, $CH_2C\underline{H}_3$) ppm; ^{13}C NMR (DMSO-d_6, 75 MHz, 300 K): δ 128.5 (C^1 and C^2), 121.7 ($C(\underline{C}N)_2$), 121.1 ($C(\underline{C}N)_2$), 119.4 (C^3), 54.9 (t, $J = 3.9$ Hz, $N(\underline{C}H_3)_4$), 47.2 ($\underline{C}H_2CH_3$), 24.4 ($\underline{C}(CN)_2$), 14.7 ($CH_2\underline{C}H_3$) ppm; IR (ATR): $\nu = 2185$ (vs) (CN), 2158 (vs) (CN), 2127 (w) (CN), 1927 (m) (cyclopropenyl) cm^{-1}; MS (ESI): positive mode: $m/z = 74.13$ (NMe_4), negative mode: $m/z = 235.90$ (cyclopropanide anion); elemental analysis calcd (%) for $C_{17}H_{22}N_6$: C 65.78, H 7.14, N 27.07; found: C 65.40, H 6.89, N 27.22.

Crystallographic data

Deposition Numbers 2164373 (**6·TDA**), 2164371 (**6·K**), 2164372 (**6-rad**), 2164369 ([**6·6-rad**]$_n$) and 2164375 (**σ-[6-rad]**$_2$) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: carbene ligands · cyclopropenium salts · radicals · density functional calculations · EPR measurements

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