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EDGE ARTICLE

The curious case of a sterically crowded Stenhouse salt

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We report a peculiar Stenhouse salt. It does not evolve into cyclopentenones upon basification, due to the steric hindrance of its bulky stable carbene patterns. This allowed for the observation and characterization of the transient open-chain neutral derivative, which was isolated as its cyclized form. The latter features an unusually long reactive C-O bond (150 pm) and a rich electrochemistry, including oxidation into an air-persistent radical cation.

Introduction

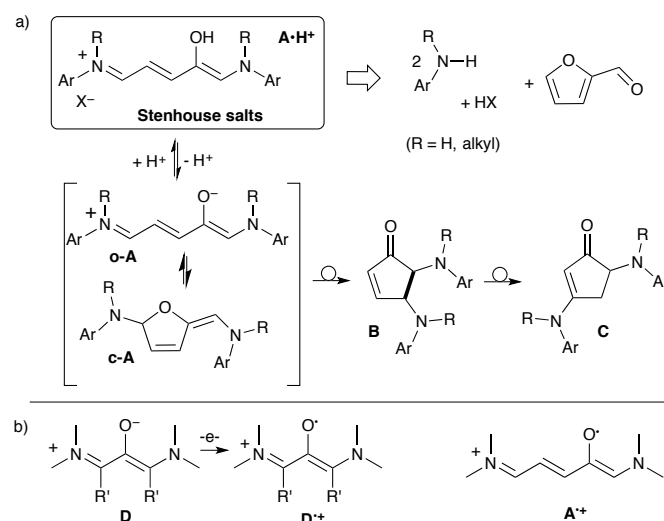
In 1850 John Stenhouse observed that furfural-containing oils deeply stain various organic tissues.¹ He later succeeded in crystallising the salt resulting from the addition of aniline to crude furfural in presence of hydrochloric acid, obtaining “a mass of beautiful iridescent fur”.² Despite this simple synthesis, the chemistry of so-called Stenhouse salts **A•H⁺** (Scheme 1) has remained fairly unexplored. Sporadic interest revivals have been limited for long by lacks of selectivity and reproducibility.³ In recent literature, Stenhouse salts are mostly invoked either as i) formal parent structures for derivative “donor-acceptor Stenhouse adducts” with photo-switching properties,⁴ ii) coloured Maillard-type products in food browning reactions⁵ or iii) elusive intermediates in the formation of cyclopentenones.^{6,7} In fact, only few conditions and substitution patterns (aryl and H, Me or indole as N,N'-substituents)^{3h,3j,3k,6,7a} have allowed for the isolation of defined salts **A•H⁺**. They easily evolve into cyclopentenones **B**, which can be substituted with a variety of nucleophiles or rearrange into a more stable isomer **C**.

The neutral deprotonated forms **A** have eluded spectroscopic observation to date. Li and Batey proposed that these intermediates exist in solution as cyclic **c-A**, whom ring opening affords less stable **o-A**, undergoing fast conrotatory electrocyclicization to give cyclopentenones **B**.^{6,7a} Note that the formation of **B** from **A•H⁺** is reversible. In some cases, the addition of acids to **B** yields back **A•H⁺**. For this reason, **B** has been sometimes misattributed to **A**, confusing further the literature.^{3,7}

Open-chain **o-A** are reminiscent of 1,3-di(amino)oxyallyls **D**. These diradicaloids have lifetimes from seconds to years in

solution at room temperature, depending on substitution patterns.^{8,9} We recently reported air-stable versions.^{8g} Compounds **D** undergo reversible electron transfers. They afford radical cations **D^{•+}**, which are usually air-persistent. Naturally, we wondered whether vinylogous open-chain **o-A** could feature similar redox behaviours. In principle the design of sterically hindered models may prevent the electrocyclicization of **A•H⁺** into **B**.

Herein, we describe the synthesis of such a Stenhouse salt featuring the extreme bulky environment provided by a cyclic (alkyl)(amino)carbene (CAAC).¹⁰⁻¹² This allowed for the unprecedented isolation of the cyclic deprotonated derivative **c-A** and the spectroscopic observation of its open-chain counterpart **o-A**. These peculiar Stenhouse-type compounds feature rich redox chemistry, including the oxidation into open-chain **A^{•+}**, a persistent paramagnetic cyanine dye.



Scheme 1. a) Stenhouse salts **A•H⁺** and their conversion into cyclopentenones. b) 1,3-di(amino)oxyallyls **D**, stabilized radical cations **D^{•+}** and putative vinylogous Stenhouse-type **A^{•+}**.

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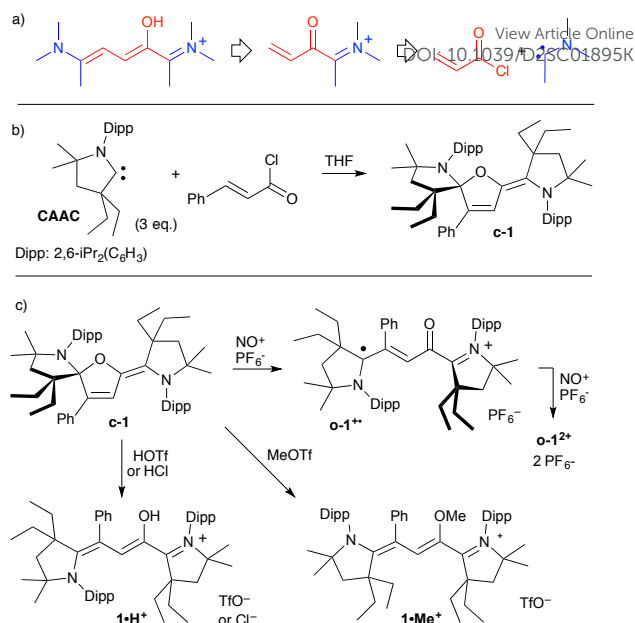


Results and discussion

Our approach towards Stenhouse derivatives from a stable carbene involves i) the formation of an acylium from the addition of a CAAC to an acryloyl chloride,¹¹ followed by ii) 1,4-addition of a second carbene to the resulting Michael acceptor, yielding a Stenhouse salt after proton migration (Scheme 2-a). As aminocarbenes are strong bases, it seemed likely that deprotonation to afford **A** would immediately follow. Therefore, we added three equivalents of CAAC to a solution of cinnamoyl chloride in THF. After work-up to remove iminium salts stemming from the protonation of one equivalent of CAAC, a pale-yellow solid was isolated in 44% yield (Scheme 2-b). A single-crystal X-ray diffraction study¹³ showed the formation of neutral close-chain Stenhouse derivative **c-1**. Data from ¹³C and ¹H NMR spectra are fully consistent. As expected from the low-symmetry of the molecule, all carbons and protons of the 2,6-di(isopropyl)phenyl group (Dipp), the gem-dimethyl and CH₂ protons of the five-membered ring of both CAAC patterns are diastereotopic. Some aromatic protons and isopropyl signals feature unusual up-field ¹H chemical shifts because the rigid structure of **c-1** forces the phenyl and a Dipp group in close vicinity of their respective shielding cones.

No trace impurity in isotropic NMR spectra could be attributed to open-chain **o-1**. However, the solid-state structure of **c-1** (Figure 1) features a remarkably long C1–O1 bond length (150.7 pm). Significant deviation from the standard value (143 pm¹⁴) is not common for C_{sp3}–O bond lengths, even in strained epoxides,¹⁵ and “extreme” lengths above 150 pm are mostly limited to some reactive oxoniums.^{16,17} We ruled out a possible artefact due to interactions or packing effects in the crystal. Indeed, DFT-optimized structures^{18,19} corroborated the experimental solid-state geometry (see supporting information), including the shorter C4–O1 distance (139.1 pm, a typical value for single C_{sp2}–O bonds¹⁴). We found that NBO formalism can account for the unusual elongation of C1–O1. Second-order perturbative energy analysis revealed a strong negative hyperconjugation of the lone pair of N1 into the low-lying $\sigma^*_{(C1-O1)}$ bond ($E_{(2)} = 21 \text{ kcal.mol}^{-1}$). As the cleavage of the weak C1–O1 bond lead to **o-1**, this suggested that the reactivity of **c-1** could mimic that of its open-chain counterpart.

Compound **c-1** is sensitive and affords highly coloured compounds when exposed to air or moisture. The hydrolysis product features a strong UV-vis absorption at 526 nm and was identified as the open-chain protonated product **1•H⁺**. It was synthesized by addition of trifluoromethanesulfonic acid to **c-1**. Stenhouse salt [**1•H⁺**][OTf] is a deep pink to violet iridescent solid with golden shinning (Scheme 2-c). Initial crystallization attempts afforded nearly-bidimensional plates (monoclinic, I2/a), which could only provide for a poorly resolved crystallographic structure determination. Thus, we synthesized [**1•H⁺**][Cl⁻] from the reaction of **c-1** with a solution of HCl in diethylether. Satisfyingly, this chloride salt crystallized as well-defined needles (monoclinic, P21/c).



Scheme 2. a) Retrosynthetic approach for the synthesis of Stenhouse salt derivatives from stable aminocarbenes; Synthesis (b) and reactivity (c) of neutral Stenhouse derivative **c-1**.

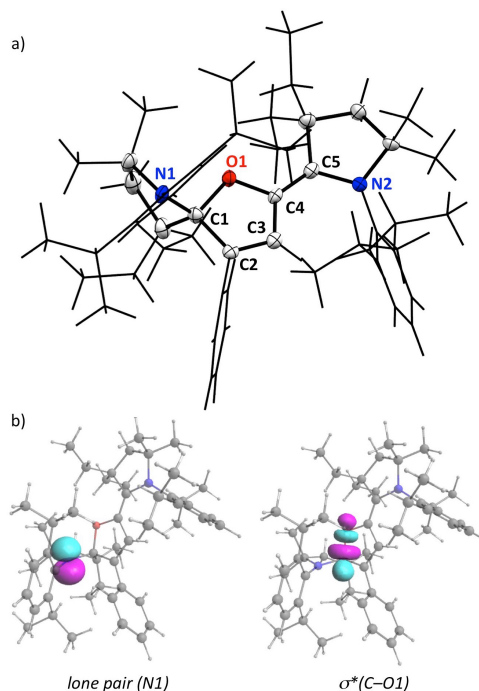


Figure 1. a) Representation of single crystal X-Ray structure of **c-1**. Wireframe display was used for clarity, with thermal ellipsoids (50% probability) shown only for selected atoms. b) Representation of relevant Natural Bond Orbitals for **c-1**.

Single-crystal X-ray crystallography confirmed the open-chain structure of **1•H⁺**. In the solid state, the chain is twisted and not fully conjugated, with one dominating resonance structure, as represented in Scheme 2. In solution, the ¹H and ¹³C spectra showed broad signals at room temperature, which



sharpened at lower temperature, suggesting a significant conformational flexibility for the π -system. As expected, salts of $\mathbf{1}\cdot\mathbf{H}^+$ yielded back $\mathbf{c-1}$ upon addition of triethylamine. Similarly, addition of methyltriflate (MeOTf) to $\mathbf{c-1}$ afforded the O-methylated Stenhouse salt $[\mathbf{1}\cdot\mathbf{Me}^+][\text{OTf}^-]$, which was fully characterized, including a single-crystal X-ray crystallography study.

EPR of aerated solutions evidenced the presence of a persistent radical, which was attributed to $\mathbf{o-1}^{\bullet}$. This was confirmed by stoichiometric preparations, either by electrolysis (see further below) or from the reaction of $\mathbf{c-1}$ with one equivalent of nitrosonium hexafluorophosphate (NOPF₆) as oxidant. The radical cation was isolated as a dark red powder (43 % yield). It is persistent in solution for hours. Note that it is rather insensitive to oxygen, with identical half-lives either under air or under argon atmosphere (about 15h in acetonitrile at room temperature). Regardless of conditions, it ultimately yielded $\mathbf{1}\cdot\mathbf{H}^+$, likely acting as a H[•] scavenger from impurities or solvents. Isotropic EPR hyperfine spectra (Figure 2) indicated a large hyperfine constant with one hydrogen atom (10 MHz) and only one nitrogen atom (11 MHz).²⁰ These values were fairly reproduced with DFT calculations (10 and 6 MHz respectively), which also showed that one CAAC moiety is orthogonal to the rest of the π -system, with no significant contribution to the singly occupied molecular orbital (SOMO). As a result, less than 5% Mulliken spin density was found on N2 and C5 (against 20% on O1, 13% on C4, 20% on C3, 13% on C2, 17% on C1 and 17% on N1).

Further oxidation of $[\mathbf{1}^{\bullet+}][\text{PF}_6^-]$ with a second equivalent of NO(PF₆) led to dication salt $[\mathbf{1}^{2+}][\text{PF}_6^-]_2$ in 60% yield. It was fully characterized, including a single-crystal X-ray crystallography study.

Cyclic voltammetry experiments unveiled a rich electrochemistry (Figure 3). Closed-chain $\mathbf{c-1}$ undergoes two successive oxidations into $\mathbf{c-1}^{\bullet+}$ ($E^\circ = -0.5$ V vs Fc/Fc⁺) and $\mathbf{c-1}^{2+}$ ($E^\circ = -0.16$ V), respectively (processes 1 and 2 on Figure 3-a). A loss of reversibility is observed at lower scan rate, which was interpreted as the result of ring opening of the oxidized species at room temperature (Figure 3-b). This hypothesis was confirmed by cyclic voltammetry studies of $[\mathbf{o-1}^{\bullet+}][\text{PF}_6^-]$. Indeed, the radical cation undergoes a reversible oxidation at $E^\circ = -0.27$ V to afford $\mathbf{o-1}^{2+}$ (process 3). The reduction wave of $\mathbf{o-1}^{\bullet+}$ is irreversible at room temperature, but becomes reversible at -30 °C (process 4, $E_{1/2} = -0.84$ V), indicating that the fast ring-closure into $\mathbf{c-1}$ follows a stepwise EC process with transient formation of neutral open-chain $\mathbf{o-1}$. Note that after a first reducing cycle in voltammograms of $[\mathbf{1}^{\bullet+}][\text{PF}_6^-]$, as $\mathbf{c-1}$ is generated, the oxidation waves of $\mathbf{c-1}$ into $\mathbf{c-1}^{\bullet+}$ (process 1) and $\mathbf{c-1}^{\bullet+}$ into $\mathbf{c-1}^{2+}$ (process 2) appear. Conversely, this also accounts for cyclic voltammograms of $\mathbf{c-1}$ at low scan-rate, which feature the reduction waves of $\mathbf{o-1}^{2+}$ into $\mathbf{o-1}^{\bullet+}$ (process 3) and of $\mathbf{o-1}^{\bullet+}$ into $\mathbf{c-1}$ (process 4).

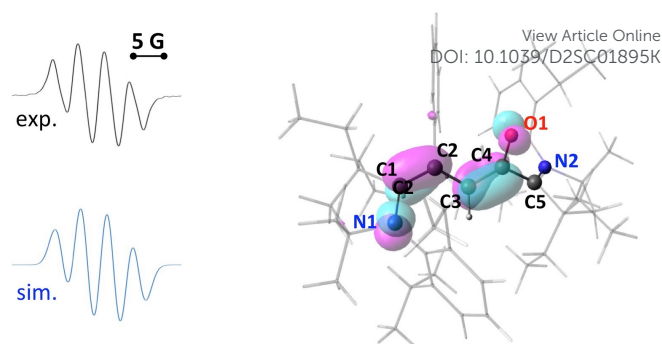


Figure 2. Left, experimental X-band EPR spectra of $\mathbf{1}^{\bullet+}$ in acetonitrile at room temperature (black); corresponding simulated spectra (blue) with the following set of parameters: line-broadening parameter $lw = 0.288$ and hyperfine coupling constants $a(^{14}\text{N}) = 11.4$ MHz and $a(^1\text{H}) = 10.1$ MHz. Right, representation of computed SOMO.

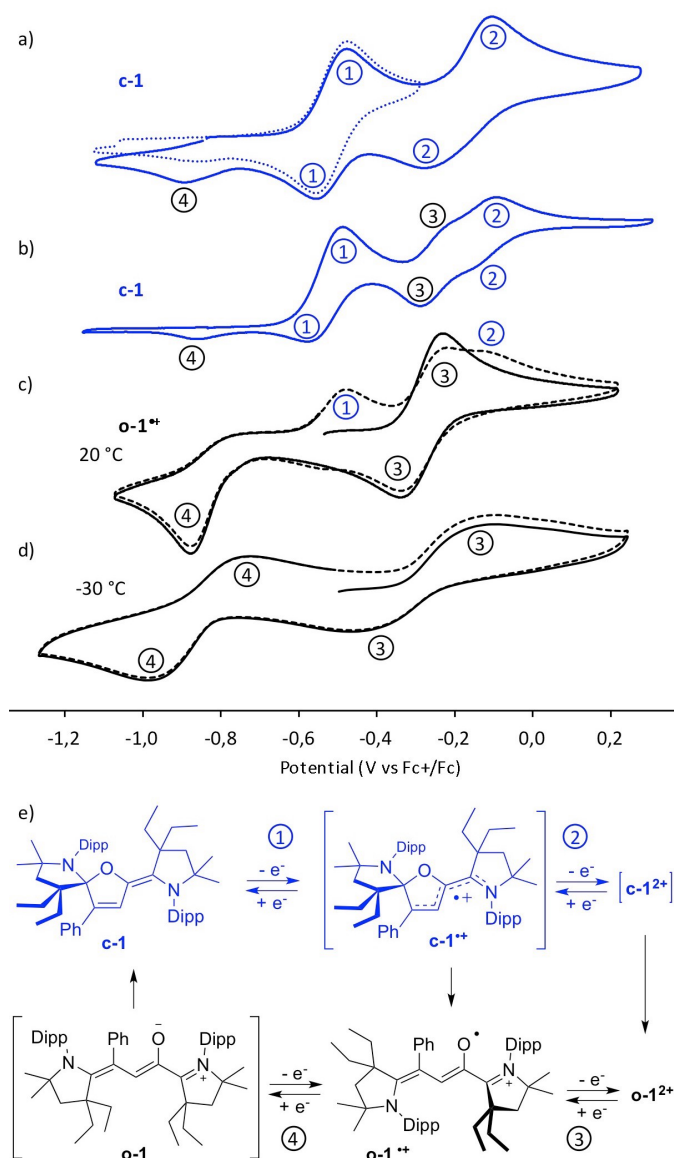


Figure 3. Cyclic voltammetry at $100 \text{ mV}\cdot\text{s}^{-1}$ rate (if not otherwise stated) with $0.1 \text{ M nBu}_4\text{NPF}_6$ electrolyte of acetonitrile solution (1 mM) of: a) $\mathbf{c-1}$, b) $\mathbf{c-1}$ at $10 \text{ mV}\cdot\text{s}^{-1}$ rate, c) $\mathbf{o-1}^{\bullet+}$ at 20 °C, d) $\mathbf{o-1}^{\bullet+}$ at -30 °C; e) corresponding electrochemical processes.



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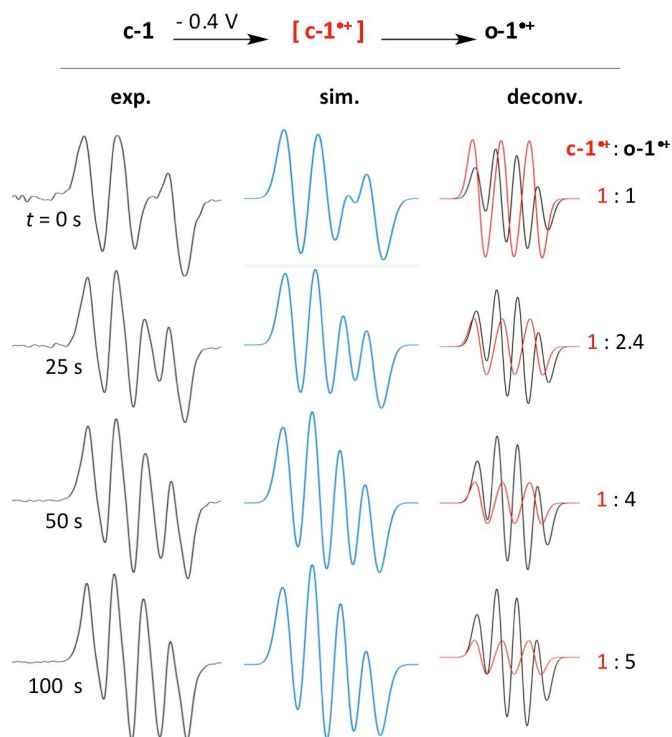
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Figure 4. Left, EPR monitoring of the electrolysis at -0.4 V of **c-1** in acetonitrile; middle, corresponding simulated spectra; right, deconvolution and respective contribution of **c-1^{•+}** (red) and **o-1^{•+}** (black) radicals to the spectra.

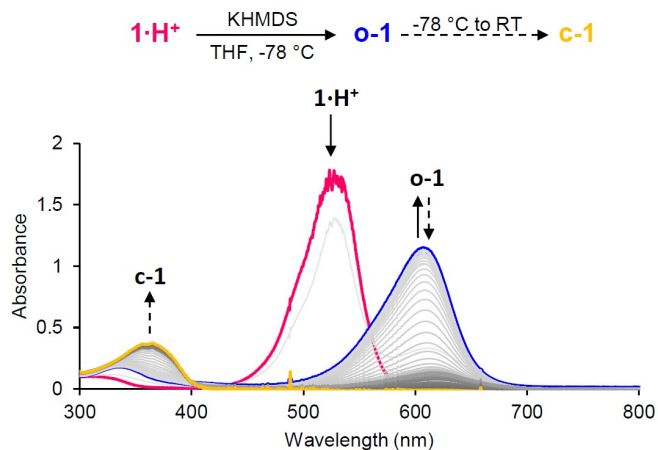


Figure 5. UV-monitoring of the addition of KHMDS to **1•H⁺** in THF.

Cyclic voltammetry experiments indicated that the ring opening of **c-1^{•+}** was slow enough to allow for its spectroscopic observation. However, UV-monitoring of the electrolysis of **c-1** couldn't clearly evidence the transient formation of this

radical. We realized that characteristic signals for **c-1^{•+}** must be hidden by the spectra of **o-1^{•+}**. Indeed TD-DFT calculations predicted very similar absorptions for both radicals (**c-1^{•+}**, 560 and 450 nm; **o-1^{•+}**, 630 and 430 nm). Thus, we turned to the in situ EPR-monitoring of the electrolysis of **c-1** at -0.4 V with an in-house device (see supporting information). We observed the formation of a transient radical with **o-1^{•+}** (Figure 4). Note that DFT calculations predicted a simple hyperfine structure for the isotropic EPR spectra of **c-1^{•+}** (with only a significant coupling constant of 13 MHz with N2. Accordingly, EPR spectra of the mixtures could be fitted with a close value (15.5 MHz). Importantly, electrochemical data also showed that the spectroscopic observation of neutral open-chain **o-1**, an elusive derivative for Stenhouse salts to date, could be possible at low temperature. Thus, we performed the addition of a strong base (potassium hexamethyldisilazide, KHMDS) to a THF solution of **1•H⁺** at -78 °C. UV-monitoring indicated an instantaneous reaction with the formation of a deep blue compound (Figure 5). The observation of a strong absorption at 610 nm matched the TD-DFT predictions for **o-1** (608 nm; $\pi_{\text{HOMO}} \rightarrow \pi_{\text{LUMO}}^*$). This band gradually disappeared upon warming to room temperature, as the characteristic band for **c-1** at 358 nm grew.

Conclusions

The basification of **1•H⁺** yields neutral spirocyclic **c-1**. Such hydrofurans have been previously only considered as elusive intermediates on the route from Stenhouse salts to cyclopentenones. Molecule **c-1** features a remarkably long C–O bond (150.7 pm), typical of those in reactive oxoniums. NBO analysis indicates a strong π -back donation of the lone pair of an amino group into the σ_{CO}^* orbital, thus accounting for the unusual elongation and easy cleavage of this bond. Neutral **c-1** can undergo two reversible oxidations affording open-chain radical cation **o-1^{•+}** and dication **o-1²⁺**. All transient forms of **c-1** (**c-1^{•+}** and **c-1²⁺**, as well as zwitterionic **o-1**) could be characterized prior to their respective ring opening or closure. Open-chain derivatives of **1** stand out among the usual cyanine polymethines.²¹ Indeed, the electrochemistry of typical representatives of this large family of organic dyes is mostly limited to one electron-oxidation, yielding short-lived radical dications followed by their fast dimerization or decay.²² This is in marked contrast with the rich redox behaviour of derivatives **1**. For instance cyanine-based radical **o-1^{•+}** is air-persistent and its oxidation affords stable dication **o-1²⁺**. Upon one-electron reduction, the deep-red radical **o-1^{•+}** is reversibly switched into yellow hydrofuran **c-1**. In turn, reversible protonation can switch **c-1** into the deep-pink cyanine **1•H⁺**.



The steric hindrance of the CAAC pattern of the novel Stenhouse derivatives has manifold implications. As already mentioned, it forbids the cyclisation into the corresponding cyclopentenone. It also considerably slows down conformational evolution of the derivatives, as demonstrated by fluxional ^1H NMR spectra of $\mathbf{1}\cdot\text{H}^+$ and $\mathbf{1}\cdot\text{Me}^+$ at room temperature. It is likely for the same reason that the ring-opening of $\mathbf{c}\text{-}\mathbf{1}^{*+}$ and $\mathbf{c}\text{-}\mathbf{1}^{2+}$ and ring-closure of $\mathbf{o}\text{-}\mathbf{1}$ are remarkably slow intramolecular processes (at least a few seconds at room temperature). Furthermore, steric hindrance prevent optimal conjugation of open-chain derivatives of $\mathbf{1}$, which all feature twisted π -systems. Thus, it is clear that fine-tuning of sterics will significantly impact the electronic, spectroscopic and electrochemical properties of the compounds. We envision that the variety of available stable N-heterocyclic carbenes will allow for the development of a large and diverse family of novel switchable redox-active cyanine dyes.

Author contributions

DM and ETM co-wrote the paper, conceived and designed the study. VT, FM, NT, SS, DM and ETM performed the chemical experiments and analysed the data. DM performed the DFT studies. JP performed the crystallographic studies. All authors discussed the results and commented on the manuscript.

Conflicts of interest

"There are no conflicts to declare".

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Notes and references

- 1 J. Stenhouse, *Liebigs Ann.*, 1850, **74**, 278-297.
- 2 J. Stenhouse, *Liebigs Ann.*, 1870, **156**, 197-205.
- 3 (a) W. König, K. Hey, F. Schulze, E. Silberkweit and K. Trautmann, *Ber. Deutsh. Chem. Gesell. B*, 1934, **67**, 1274-1296; (b) G. Williams and C. L. Wilson, *J. Chem. Soc.*, 1942, 506-507; (c) A. P. Dillon and K. G. Lewis, *Tetrahedron*, 1969, **25**, 2035-2039; (d) K. G. Lewis and C. E. Mulquiney, *Aust. J. Chem.*, 1970, **23**, 2315-2323; (e) K. G. Lewis, *Aust. J. Chem.*, 1973, **26**, 893-897; (f) K. G. Lewis and C. E. Mulquiney, *Tetrahedron*, 1977, **33**, 463-475; (g) K. G. Lewis and C. E. Mulquiney, *Aust. J. Chem.*, 1979, **32**, 1079-1092; (h) K. Honda, H. Komizu and M. Kawasaki, *J. Chem. Soc., Chem. Commun.*, 1982, 253-254; (i) B. R. d'Arcy, K. G. Lewis and C. E. Mulquiney, *Aust. J. Chem.*, 1985, **38**, 953-965; (j) P. Safar, J. Kováč, *Collect. Czech. Chem. Commun.*, 1989, **54**, 2425-2432; (k) H. S. Patel and G. H. Majmudar, *Eur. Polym. J.*, 1991, **27**, 89-92.
- 4 (a) M. M. Lerch, W. Szymański and B. L. Feringa, *Chem. Soc. Rev.*, 2018, **47**, 1910-1937; (b) S. Helmy, F. A. Leibfarth, S. Oh, J. E. Poelma, C. J. Hawker and J. Read de Alaniz, *J. Am. Chem. Soc.*, 2014, **136**, 8169-8172; (c) S. Helmy, S. Oh, F. A. Leibfarth, C. J. Hawker and J. Read de Alaniz, *J. Org. Chem.*, 2014, **79**, 11316-11329.
- 5 T. Hofmann, *J. Agric. Food Chem.*, 1998, **46**, 932-940.
- 6 R. F. A. Gomes, J. A. S. Coelho and C. A. M. Afonso, *Chem. Eur. J.*, 2018, **24**, 9170-9186.
- 7 (a) S.-W. Li and R. A. Batey, *Chem. Commun.*, 2007, **43**, 3759-3761; (b) A. Procopio, P. Costanzo, M. Curini, M. Nardi, M. Oliverio and G. Sindona, *ACS Sustainable Chem. Eng.*, 2013, **1**, 541-544; (c) K. Griffiths, C. W. D. Gallop, A. Abdul-Sada, A. Vargas, O. Navarro and G. E. Kostakis, *Chem. Eur. J.*, 2015, **21**, 6358-6361; (d) K. Griffiths, P. Kumar, J. D. Mattock, A. Abdul-Sada, M. B. Pitak, S. J. Coles, O. Navarro, A. Vargas and G. E. Kostakis, *Inorg. Chem.*, 2016, **55**, 6988-6994; (e) M. S. Estevão, R. J. V. Martins and C. A. M. Afonso, *J. Chem. Educ.* 2017, **94**, 1587-1589; (f) R. F. A. Gomes, N. R. Esteves, J. A. S. Coelho and C. A. M. Afonso, *J. Org. Chem.*, 2018, **83**, 7509-7513; (g) M. L. Di Gioia, M. Nardi, P. Costanzo, A. De Nino, L. Maiuolo, M. Oliverio and A. Procopio, *Molecules*, 2018, **23**, 1891-1904; (h) S. I. Sampani, A. McGown, A. Vargas, A. Abdul-Sada, G. J. Tizzard, S. J. Coles, J. Spencer and G. E. Kostakis, *J. Org. Chem.*, 2019, **84**, 6858-6867; (i) J. G. Pereira, J. P. M. António, R. Mendonça, R. F. A. Gomes and C. A. M. Afonso, *Green Chem.*, 2020, **22**, 7484-7490; (j) K. Peewasan, M. P. Merkel, O. Fuhr and A. K. Powell, *Dalton Trans.*, 2020, **49**, 2331-2336; (k) T. B. Shah, R. S. Shiny, R. B. Dixit and B. C. Dixit, *J. Saud. Chem. Soc.*, 2014, **18**, 985-992.
- 8 (a) D. Martin, C. E. Moore, A. L. Rheingold and G. Bertrand, *Angew. Chem. Int. Ed.*, 2013, **52**, 7014-7017; (b) T. Schulz, C. Farber, M. Leibold, C. Bruhn, W. Baumann, D. Selent, T. Porsch, M. C. Holthausen and U. Siemeling, *Chem. Commun.* 2013, **49**, 6834; (c) V. Regnier and D. Martin, *Organic Chemistry Frontiers*, 2015, **2**, 1536-1545; (d) V. Regnier, F. Molton, C. Philouze and D. Martin, *Chem. Commun.*, 2016, **52**, 11422-11425; (e) M. Devillard, V. Regnier, M. Tripathi and D. Martin, *J. Mol. Struct.*, 2018, **1172**, 3-7; (f) M. Tripathi, V. Regnier, Z. Ziani, M. Devillard, C. Philouze and D. Martin, *RSC Advances*, 2018, **8**, 38346 - 38350; (g) E. Tomás-Mendivil, M. Devillard, V. Regnier, J. Pecaut and D. Martin, *Angew. Chem. Int. Ed.*, 2020, **59**, 11516-11520.
- 9 See also: (a) U. Siemeling, C. Farber, C. Bruhn, M. Leibold, D. Selent, W. Baumann, M. von Hopffgarten, C. Goedecke and G. Frenking, *Chem. Sci.*, 2010, **1**, 697; (b) S. D. Ursula and U. Radius, *Organometallics*, 2017, **36**, 1398; (c) G. Kuzmanich, F. Spänig, C. K. Tsai, J. M. Um, R. M. Hoekstra, K. N. Houk, D. M. Guldi and M. A. Garcia-Garibay, *J. Am. Chem. Soc.*, 2011, **133**, 2342.
- 10 (a) V. Lavallo, Y. Canac, C. Prasang, B. Donnadiu and G. Bertrand, *Angew. Chem. Int. Ed.*, 2005, **44**, 5705; (b) M. Melaimi, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2010, **49**, 8810-8849; (c) M. Soleilhavoup and G. Bertrand, *Acc. Chem. Res.*, 2015, **48**, 256-266; (d) S. Roy, K. C. Mondal and H. W. Roesky, *Acc. Chem. Res.*, 2016, **49**, 357-369; (e) U. S. D. Paul and U. Radius, *Eur. J. Inorg. Chem.*, 2017, 3362-3375; (f) M. Melaimi, R. Jazzar, M. Soleilhavoup and G. Bertrand, *Angew. Chem., Int. Ed.*, 2017, **56**, 10046-10068.
- 11 CAAC-based organic radicals: (a) J. K. Mahoney, D. Martin, C. Moore, A. Rheingold and G. Bertrand, *J. Am. Chem. Soc.*, 2013, **135**, 18766-18769; (b) L. Jin, M. Melaimi, L.L. Liu and



- G. Bertrand, *Org. Chem. Front.*, 2014, **1**, 351-354; (c) Y. Li, K. C. Mondal, P. P. Samuel, H. Zhu, C. M. Orben, S. Panneerselvam, B. Dittrich, B. Schwederski, W. Kaim, T. Mondal, D. Koley and H. W. Roesky, *Angew. Chem., Int. Ed.*, 2014, **53**, 4168-4172; (d) J. K. Mahoney, D. Martin, F. Thomas, C. Moore, A. L. Rheingold and G. Bertrand, *J. Am. Chem. Soc.*, 2015, **137**, 7519-7525; (e) S. Styra, M. Melaimi, C. E. Moore, A. L. Rheingold, T. Augenstein, F. Breher and G. Bertrand, *Chem. Eur. J.*, 2015, **21**, 8441-8446; (f) D. Munz, J. Chu, M. Melaimi and G. Bertrand, *Angew. Chem., Int. Ed.*, 2016, **55**, 12886-12890; (g) J. K. Mahoney, R. Jazzar, G. Royal, D. Martin and G. Bertrand, *Chem. Eur. J.*, 2017, **23**, 6206-6212; (h) M. M. Hansmann, M. Melaimi and G. Bertrand, *J. Am. Chem. Soc.*, 2017, **139**, 15620-15623; (i) M. M. Hansmann, M. Melaimi and G. Bertrand, *J. Am. Chem. Soc.*, 2018, **140**, 2206-2213; (j) P. W. Antoni and M. M. Hansmann, *J. Am. Chem. Soc.*, 2018, **140**, 14823-14835; (k) P. W. Antoni, T. Bruckhoff, and M. M. Hansmann, *J. Am. Chem. Soc.*, 2019, **141**, 9701-9711; (l) V. Regnier, E. A. Romero, F. Molton, R. Jazzar, G. Bertrand and D. Martin, *J. Am. Chem. Soc.*, 2019, **141**, 1109-1117; (m) J. Messelberger, A. Grünwald, S. J. Goodner, F. Zeilinger, P. Pinter, M. E. Miehlich, F. W. Heinemann, M. M. Hansmann and D. Munz, *Chem. Sci.*, 2020, **11**, 4138-4149.
- 12 For stable organic radicals based on other types of N-heterocyclic carbenes, see also: (a) J. Back, J. Park, Y. Kim, H. Kang, Y. Kim, M. J. Park, K. Kim and E. Lee, *J. Am. Chem. Soc.*, 2017, **139**, 15300-15303; (b) C. L. Deardorff, R. E. Sikma, C. P. Rhodes and T. W. Hudnall, *Chem. Commun.* **2016**, *52*, 9024-9027; (c) L. Y. M. Eymann, A. G. Tskhovrebov, A. Sienkiewicz, J. L. Bila, I. Zikhovic, H. M. Ronnow, M. D. Wodrich, L. Vannay, C. Corminboeuf, P. Pattison, E. Solari, R. Scopelliti and K. Severin, *J. Am. Chem. Soc.*, 2016, **138**, 15126-15129; (d) D. Rottschäfer, B. Neumann, H.-G. Stämmler, M. van Gastel, D. M. Andrada and R. S. Ghadwal, *Angew. Chem., Int. Ed.*, 2018, **57**, 4765-4768; (e) N. M. Gallagher, H.-Z. Ye, S. Feng, J. Lopez, Y. G. Zhu, T. Van Voorhis, Y. Shao-Horn and J. A. Johnson, *Angew. Chem., Int. Ed.*, 2020, **59**, 3952-3955; (f) Y. Kim, J. E. Byeon, G. Y. Jeong, S. S. Kim, H. Song, and E. Lee, *J. Am. Chem. Soc.*, 2021, **143**, 23, 8527-8532; (g) J. Zhao, X. Li and Y.-F. Han, *J. Am. Chem. Soc.*, 2021, **143**, 14428-14432; (h) L. Delfau, S. Nichilo, F. Molton, J. Broggi, E. Tomás-Mendivil and D. Martin, *Angew. Chem. Int. Ed.* 2021, **60**, DOI: 10.1002/anie.202111988.
- 13 CCDC 2163356-2163359 contains the supplementary crystallographic data for this paper. These data are provided free of charge by the Cambridge Crystallographic Data Centre.
- 14 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc. Perkin Trans. II*, 1987, S1.
- 15 See for example: A. J. Leyhane and M. L. Snapper, *Org. Lett.*, 2006, **8**, 5183-5186.
- 16 G. Gunbas, N. Hafezi, W. L. Sheppard, M. M. Olmstead, I. V. Stoyanova, F. S. Tham, M. P. Meyer and M. Mascals, *Nature Chem.*, 2012, **4**, 1018-1023.
- 17 A long C–O bond was also reported in strained acenaphthofurans: Y. Uchimura, T. Shimajiri, Y. Ishigaki, R. Katoono and T. Suzuki, *Chem. Commun.*, 2018, **54**, 10300-10303.
- 18 Calculations were performed with the Gaussian suite of programs: Gaussian09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, et al., Gaussian, Inc., Wallingford CT, 2009. See Supporting Information for complete citation.
- 19 If not otherwise stated, calculations were carried out at the B3LYP/6-311g(d,p) level of theory with PCM model for acetonitrile and Grimme's D3 empirical dispersion: S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
 View Article Online
DOI: 10.1039/D2SC01895K
- 20 Experimental values for isotropic hyperfine constants were extracted from EPR spectra by fitting with the EasySpin simulation package: S. Stoll and A. Schweiger, *J. Magn. Reson.* 2006, **178**, 42-55.
- 21 For general reviews on cyanine dyes: (a) A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra and G. B. Behera, *Chem. Rev.*, 2000, **100**, 1973-2012; (b) J. L. Bredas, C. Adant, P. Tackx, A. Persoons and B. M. Pierce, *Chem. Rev.* 1994, **94**, 243-278.
- 22 (a) R. Lenhard and A. D. Cameron, *J. Phys. Chem.*, 1993, **97**, 4916-4925; (b) J. E. H. Buston, F. Marken and H. L. Anderson, *Chem. Commun.*, 2001, **37**, 1046-1047; (c) J. L. Lyon, D. M. Eisele, S. Kirstein, J. P. Rabe, D. A. Vanden Bout and K. J. Stevenson, *J. Phys. Chem. C*, 2008, **112**, 1260-1268. (d) J. Lenhard and R. Parton, *J. Am. Chem. Soc.*, 1987, **109**, 5808-5813; (e) R. Parton and J. Lenhard, *J. Org. Chem.*, 1990, **55**, 49-57.

