Electronic Supplementary Information

Rethinking Aromaticity of Reduced Thienoquinoids: Insights from an S-Pechmann Dye Dianion

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1. Experimental Details for the Synthesis

General. Melting points (mp) were determined with a Yanaco MP-S3 instrument. ¹H and ¹³C{¹H} NMR spectra were recorded with a Bruker AVANCE III 500 MHz spectrometer (500 MHz for ¹H and 126 MHz for ¹³C). The chemical shifts in ¹H NMR spectra are reported in δ ppm using the residual protons of the solvents, CHCl₃ 7.26 ppm and THF 3.58 ppm as an internal standard, and those in ¹³C NMR spectra are reported using the solvent signals of CDCl₃ 77.16 ppm and THF 67.21 ppm. Mass spectra were measured with a Bruker timsTOF (IMS-QTOF) system with the ionization method of APCI. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm thickness of silica gel 60F₂₅₄ (Merck). Flash chromatography was performed with a Biotage Isolera Selekt instrument using normal-phase silica gel of PSQ60B (Fuji Silysia Chemicals) or Biotage® Sfär HC D (Biotage). Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Anhydrous THF was purchased from Kanto Chemicals and further purified by Glass Contour Solvent Systems. All reactions were performed under a nitrogen atmosphere unless stated otherwise.



5,5'-Bis(4-*tert***-butylphenyl)-3,3'-bithiophene (4).** A mixture of 5,5'-dibromo-3,3'-bithiophene (3, 323 mg, 1.00 mmol), 4-(*tert*-butyl)phenylboronic acid (430 mg, 2.42 mmol), K₂CO₃ (693 mg, 5.01 mmol), and Pd(PPh₃)₄ (55.6 mg, 48.1 µmol) in THF (20 mL)/H₂O (2.0 mL) was stirred at 80 °C for 20 h. After cooling to room temperature, the reaction mixture was quenched with a saturated aqueous solution of NH₄Cl (20 mL). The volatiles were removed under reduced pressure, and the resulting residue was dissolved in CHCl₃ (20 mL). The biphasic mixture was separated, and the aqueous phase was extracted with CHCl₃ (15 mL \times 3). The organic phase and the subsequent CHCl₃ extracts were combined, washed with brine (30 mL), dried over Na₂SO₄, and filtered. The solvents were removed under reduced pressure to afford a crude product, which was purified by silica gel column chromatography using hexane/ethyl acetate = 1/1 as eluent ($R_{\rm f} = 0.56$), yielding 404 mg of **4** as white solids (0.939 mmol, 94% yield). Mp: 207.4–208.4 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.36 (s, 18H), 7.32 (d, 2H, J = 1.4 Hz), 7.43 (d, 4H, J = 8.3 Hz), 7.51 (d, 2H, J = 1.4 Hz), 7.59 (d, 4H, J = 8.3 Hz). ¹³C {¹H} NMR (126 MHz, CDCl₃): δ 31.43, 34.79, 118.99, 121.92, 125.79, 126.00, 131.63, 138.22, 145.17, 151.07. HRMS (APCI): m/z Calcd. for C₂₈H₃₀S₂: 431.1862 ([M+H]⁺). Obsd. 431.1859.



5,5'-Bis(4-*tert***-butylphenyl)-3,3'-bi[thiophen-3(2***H***)-ylidene]-2,2'-dione** (**1a**). To a solution of **4** (431 mg, 1.00 mmol) in anhydrous THF (10.0 mL), *n*-BuLi in hexane (1.6 M, 1.56 mL, 2.50 mmol) was added dropwise at -78 °C over 1 min. The reaction mixture was stirred at the same temperature for 1 h, followed by the addition of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.690 mL, 3.00 mmol) in one portion. The resulting mixture was allowed to warm gradually to ambient temperature and stirred for an additional 21 h. Methanol (2 mL) was added to quench the reaction, and the volatiles were removed under reduced pressure. The residual solids were suspended in CH₂Cl₂, and the resulting precipitates were removed by vacuum filtration through a PTFE membrane filter. The volatile solvents were removed from the filtrate to give crude solids containing **5**, which were subjected to the subsequent oxidation reaction without further purification.

The crude solids containing **5** was dissolved in CH₂Cl₂ (10 mL)/acetone (10 mL)/H₂O (10 mL), and Oxone[®] (2KHSO₅•K₂SO₄•KHSO₄, 3.07 g, 5.00 mmol) was added. The mixture was at ambient temperature for 24 h. After cooling to 0 °C, the reaction was quenched with a saturated aqueous solution of Na₂SO₃ (20 mL). The volatiles were removed under reduced pressure, and the resulting residue was dissolved in CH₂Cl₂ (100 mL). The biphasic mixture was separated, and the aqueous layer was extracted with CH₂Cl₂ (15 mL × 3). The organic phase and the subsequent CH₂Cl₂ extracts were combined, washed with brine (50 mL), dried over Na₂SO₄, and filtered. The solvents were removed under reduced pressure. The crude product was purified by silica gel column chromatography using hexane/CHCl₃ = 1/1 as eluent (R_f = 0.61) to afford 186 mg of **1a** as black solids with metallic luster (0.404 mmol, 40% yield). Mp: 316.2–317.1 °C. ¹H NMR (500 MHz, CDCl₃): δ 1.35 (s, 18H), 7.48 (d, 4H, J = 8.6 Hz), 7.63 (d, 4H, J = 8.6 Hz), 8.28 (s, 2H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ 31.25, 35.29, 116.88, 126.29, 127.01, 130.43, 136.04, 150.63, 155.33, 195.23. HRMS (APCI): *m/z* Calcd. for C₂₈H₂₈O₂S₂: 461.1603 ([*M*+H]⁺). Obsd. 461.1601.



Chemical Reduction of 1a²⁻.

1. NMR Measurement. In an argon-filled glove box, THF- d_8 (1.0 mL), which was dehydrated over potassium and degassed by repeating the freeze-pump-thaw cycles three times in advance, was added to the flask charged with **1a** (9.2 mg, 0.020 mmol) and KC₈ (6.0 mg, 0.044 mmol). After stirring at ambient temperature for 14 h, the color of the reaction mixture changed from blue to yellowish brown. After vacuum filtration through a PTFE membrane filter to remove the precipitates containing graphite, the resulting filtrate containing **1a**^{2–} was subjected to the NMR measurements. ¹H NMR (500 MHz, THF- d_8): δ 1.29 (s, 18H), 6.86 (s, 2H), 7.15 (d, 4H, J = 8.4 Hz), 7.19 (d, 4H, J = 8.4 Hz). ¹³C{¹H} NMR (126 MHz, THF- d_8): δ 31.69, 34.61, 109.31, 115.31, 112.85, 125.11, 125.39, 136.20, 145.14, 175.27.

2. Preparation of single crystals suitable for the X-ray crystallographic analysis. Chemical reduction of 1a (9.2 mg, 0.020 mmol) with KC₈ (5.4 mg, 0.040 mmol) in degassed and anhydrous THF (1.0 mL) was conducted in a similar manner as described above. Into the resulting solution containing $1a^{2-}$, a solution of [2.2.2]cryptand (10.0 mg, 26.5 µmol) in hexane (1.0 mL) was slowly diffused at ambient temperature to afford dark red crystals of the dianion [(K[2.2.2]cryptand)⁺]₂ $1a^{2-}$.

2. X-ray Crystallographic Data

X-ray Data Collection of 1a. Blue needle-shaped single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of hexane into a solution of **1a** in THF at an ambient temperature. Intensity data were collected at 100 K on synchrotron radiation ($\lambda = 0.414$ Å) at the BL02B1 beamline in SPring-8 (JASRI). A total of 148754 reflections were measured with the maximum 2θ angle of 31.2° , of which 8198 were independent reflections ($R_{int} = 0.0672$). The crystal data are as follows: C₂₈H₂₈O₂S₂; FW = 460.62, crystal size = $0.010 \times 0.010 \times 0.010$ mm³, orthorhombic, *Pbca* (#61), *a* = 7.83060(10) Å, *b* = 30.1726(3) Å, *c* = 30.2525(3) Å, *a* = 90°, $\beta = 90^{\circ}$, $\gamma = 90^{\circ}$, *V* = 7147.75(14) Å³, *Z* = 12, *D*_c = 1.284 g cm⁻³, $\mu = 0.068$ mm⁻¹, $R_1 = 0.0332$ ($I > 2\sigma(I)$), $wR_2 = 0.1062$ (all data), GOF = 1.035. CCDC 2446608 contains the supplementary crystallographic data for this compound. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC).

X-ray Data Collection of $[(K[2.2.2]cryptand)^+]_21a^{2-}$. Dark-red needle-shaped crystals were grown by slow diffusion of a hexane solution of [2.2.2]cryptand into a THF solution of $1a^{2-}$ as described above. Intensity data were collected at 100 K on synchrotron radiation ($\lambda = 0.414$ Å) at the BL02B1 beamline in SPring-8 (JASRI). A total of 33615 reflections were measured with the maximum 2θ angle of 30.0°, of which 7255 were independent reflections ($R_{int} = 0.0724$). The crystal data are as follows: $C_{28}H_{108}K_2N_4O_{15}S_2$; FW = 1363.90, crystal size = 0.010 × 0.010 × 0.010 mm³, triclinic, *P*-1 (#2), *a* = 11.4080(6) Å, *b* = 12.0912(8) Å, *c* = 14.9019(8) Å, *a* = 73.723(5)°, β = 69.097(5)°, γ = 70.197(6)°, *V* = 1776.7(2) Å³, Z = 2, $D_c = 1.275$ g cm⁻³, $\mu = 0.071$ mm⁻¹, $R_1 = 0.0413$ ($I > 2\sigma(I)$), $wR_2 = 0.1014$ (all data), GOF = 1.025. CCDC 2446610 contains the supplementary crystallographic data for this compound. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC).

X-ray Data Collection of 4. Colorless platelet single crystals suitable for X-ray crystallographic analysis were obtained by slow diffusion of hexane into a solution of **4** in CHCl₃ at an ambient temperature. Intensity data were collected at 100 K on synchrotron radiation ($\lambda = 0.413$ Å) at BL02B1 beamline in SPring-8 (JASRI). A total of 15898 reflections were measured with the maximum 2θ angle of 31.1°, of which 2647 were independent reflections ($R_{int} = 0.0740$). The crystal data are as follows: C₂₈H₃₀S₂; FW = 430.64, crystal size = 0.100 × 0.100 × 0.010 mm³, monoclinic, *P*2₁/*c* (#14), *a* = 13.2850(8) Å, *b* = 6.0285(2) Å, *c* = 15.0211(6) Å, $\alpha = 90^{\circ}$, $\beta = 105.958(5)^{\circ}$, $\gamma = 90^{\circ}$, *V* = 1156.66(10) Å³, *Z* = 2, *D*_c = 1.236 g cm⁻³, $\mu = 0.067$ mm⁻¹, *R*₁ = 0.0394 (*I* > 2 σ (*I*)), *wR*₂ = 0.1100 (all data), GOF = 1.056. CCDC 2446609 contains the supplementary crystallographic data for this compound. This data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC).



Fig. S1. X-ray crystal structure of **1a** shown as thermal ellipsoid plots at 50% probability level: black, carbon; white, hydrogen; red, oxygen; yellow, sulfur. The crystal lattice consists of two crystallographically independent units, A and B.



Fig. S2. X-ray crystal structure of $[(K[2.2.2]cryptand)^+]_2\mathbf{1a}^{2-}$ shown as thermal ellipsoid plots at the 50% probability level: black, carbon; white, hydrogen; red, oxygen; yellow, sulfur. One THF molecule is included in each crystal lattice.



Fig. S3. X-ray crystal structure of **4** shown as thermal ellipsoid plots at the 50% probability level: black, carbon; white, hydrogen; yellow, sulfur.

Bond Length Analysis

Table S1. Selected bond lengths of 1a, $[(K[2.2.2]cryptand)^+]_2 1a^{2-}$, and 4 in their crystal structures.



h e e el	bond length / Å				
bona	1a (A)	1a (B)	1a ²⁻	4	
C2-C16	1.3822(15)	1.3833(19)	1.486(3)	1.478(2)	
C1-C2	1.5051(12)	1.5042(12)	1.421(3)	1.3807(19)	
C2-C3	1.4341(13)	1.4322(12)	1.411(2)	1.4391(17)	
C3-C4	1.3690(13)	1.3693(13)	1.380(2)	1.3790(18)	
C4-C5	1.4649(13)	1.4629(13)	1.456(2)	1.4791(17)	
C5-C6	1.4018(13)	1.4042(13)	1.413(2)	1.3977(19)	
C5-C7	1.4062(13)	1.4022(13)	1.407(3)	1.396(2)	
C6-C8	1.3898(14)	1.3893(14)	1.396(3)	1.40046(19)	
C7-C9	1.3894(14)	1.3903(14)	1.392(3)	1.396(2)	
C8-C10	1.3915(14)	1.3976(14)	1.402(3)	1.394(2)	
C9-C10	1.4102(14)	1.4023(14)	1.402(3)	1.3985(19)	
C1-O1	1.2123(12)	1.2137(12)	1.261(2)		
C1-S1	1.7923(10)	1.7961(10)	1.8387(18)	1.7217(14)	
C4-S1	1.7654(9)	1.7646(9)	1.7544(19)	1.7396(13)	
C15-C16	1.5060(12)	—	_		
C16-C17	1.4310(13)	—	_		
C17-C18	1.3680(13)	—	_		
C18-C19	1.4623(12)	_	-		
C19-C20	1.4060(13)	_	-		
C19-C21	1.4038(13)	_	-		
C20-C22	1.3878(14)	_	-		
C21-C23	1.3928(13)	_	-		
C22-C24	1.3992(14)	_	-		
C23-C24	1.4021(14)	_	-		
C15-O2	1.2120(12)	_	-		
C15-S2	1.7970(10)	_	_		
C18-S2	1 7642(9)	_	_		

Calculations of the HOMA Values

The harmonic oscillator model of aromaticity $(HOMA)^{[S1]}$ of **1a**, and $[(K[2.2.2]cryptand)^+]_2 \mathbf{1a}^{2-}$ were calculated using the X-ray crystal structures based on the following equation:

$$HOMA = 1 - \frac{\alpha}{n} \sum (R_{opt} - R_i)^2$$

where a is an empirical normalization constant ($\alpha = 257.7$, 94.09 for a C–C, C–S bond, respectively)^[S1a], *n* is the number of C–C bonds taken into summation, R opt is the optimal aromatic bond length ($R_{opt} = 1.388$ Å and 1.677 Å for a C–C and C–S bond, respectively)^[S1a] and R_i is a bond length from the X-ray crystal structures.

3. NMR Spectra of New Compounds



Fig. S4. ¹H NMR spectrum of 4 (500 MHz, CDCl₃).



Fig. S5.¹³C $\{^{1}H\}$ NMR spectrum of 4 (126 MHz, CDCl₃).



Fig. S6. ¹H NMR spectrum of 1a (500 MHz, CDCl₃).



Fig. S7. ¹³C{¹H} NMR spectrum of **1a** (126 MHz, CDCl₃).



Fig. S8. ¹H NMR spectrum of $1a^{2-}$ (500 MHz, THF- d_8).



Fig. S9. ${}^{13}C{}^{1}H$ NMR spectrum of $1a^{2-}$ (126 MHz, THF- d_8).



Fig. S10. ¹³C{¹H} NMR spectra of **1a** (top) and **1a** after the addition of two equivalents of KC₈ in THF- d_8 (bottom). The resonance assignments refer to the structure.

2D NMR Analysis

2D NMR spectra of 1a and $1a^{2-}$ were recorded with a Bruker AVANCE III 500 MHz spectrometer for the resonance assignments.



Fig. S11. 2D HSQC NMR spectra of 1a in tetrahydrofuran- d_8 .



Fig. S12. 2D HMBC NMR spectra of 1a in tetrahydrofuran-d₈.



Fig. S13. 2D HSQC NMR spectra of $1a^{2-}$ in tetrahydrofuran- d_8 .



Fig. S14. 2D HMBC NMR spectra of $1a^{2-}$ in tetrahydrofuran- d_8 .

4. Theoretical Calculations

Computational Methods. All density functional theory (DFT) calculations in this article were performed with the Gaussian16 Revision B.01 suite of programs^[S2] with default thresholds and algorithms. In order to benchmark density functionals and basis sets, the geometry optimizations for 1a and $1a^{2-}$ were carried out using density functional theory (DFT) with various density functionals (B3LYP,^[S3] CAM-B3LYP,^[S4] and ω B97X-D^[S5]) and basis sets (6-31+G(d),^[S6-7] 6-311+G(d),^[S7-8] 6-31+G(d,p), [S6, 7, 9] and 6-311+G(d,p) [S7-9]) shown in Fig. S15-18. Since the optimized structure at the ω B97X-D/6-31+G(d) level of theory showed the best agreement with the bond lengths of the crystal structure, the geometry optimizations of $1b^{2-}$, $2b^{2-}$, $1c^{2-}$, and $2c^{2-}$ were performed at the ω B97X-D/6-31+G(d) level of theory. The Cartesian coordinates for the optimized geometries of $1b^{2-}$, $2b^{2-}$, $1c^{2-}$, and $2c^{2-}$ at the ω B97X-D/6-31+G(d) level of theory were given in Tables S4-7. The nucleusindependent chemical shift (NICS)^[S10] values were calculated at the ω B97X-D/6-31+G(d) level of theory. The XY planes were set on the mean planes defined by the five- or six-membered rings. The results are summarized in Fig. 4b. The anisotropy of the current density (ACID) for the optimized geometries of $1b^{2-}$ and $2b^{2-}$ was calculated at the ω B97X-D/6-31+G(d) level of theory using the AICD software version 2.0.0.[S11] The magnetic field in the AICD calculations was chosen to be parallel to the Z-axis, which is oriented in a perpendicular direction to the paper plane and pointing towards the reader. The graphics were generated using the POV-Ray program and given in Fig. 4c. The gauge including magnetically induced current (GIMIC) for the optimized geometries of $1b^{2-}$ and $2b^{2-}$ was also calculated at the wB97X-D/6-31+G(d) level of theory.^[S12] GIMIC computations for current density integration $|\chi|$ were conducted with the external magnetic fields oriented along the normal vector of the investigated ring plane. Parameters for the GIMIC computations are illustrated in Fig. S21, using the bond between C2 and C3 of $1b^{2-}$ as an example. A rectangular integration plane of 10.0 × 4.4 Bohr is placed across the C2-C3 bond, with its midpoint located 1.32 Bohr from C2, which exactly half of the standard C-C bond length in benzene (2.64 Bohr). In addition, C4 is fixed to define a plane containing both C2 and C3. Same parameters were used for the computation of $2b^{2-}$ by using C1–C2 bond and C3 for fixing. Natural resonance theory (NRT) analysis^[S13] for $1c^{2-}$ and $2c^{2-}$ and natural population analysis (NPA)^[S14] were calculated at the ω B97X-D/6-31+G(d) level of theory with NBO 7.0 software.^[S15] The results are summarized in Fig. 5 and Tables S2-3.

Interpretation of NRT analysis: To compare the π -electron delocalization patterns in the model dianions $1c^{2-}$ and $2c^{2-}$, Natural Resonance Theory (NRT) analysis was conducted. The dominant resonance contributors and their corresponding NRT weights [%] for the model dianions $1c^{2-}$ and $2c^{2-}$, calculated at the ω B97X-D/6-31+G(d) level of theory, are shown in Figures S15 and S16, respectively. Resonance contributors with NRT weights below 2% were excluded for clarity, as an excessive number of such low-contributing structures were generated. For degenerate contributors arising from molecular symmetry, the number of equivalent resonance structures is indicated alongside their NRT weights. The individual resonance structures thus obtained were further classified into two types: Type I, in which at least one five-membered ring (highlighted in pink) exhibits aromatic character, and Type II, which lack such aromatic features. To compare the contribution of aromatic stabilization between two systems, the total NRT weight of all Type I resonance structures was calculated. Notably, in the case of the pentafulvalene dianion $2c^{2-}$, all dominant resonance contributors classified to Type I exhibit 6π aromaticity in both five-membered rings. In contrast, some of Type I structures for S-Pechmann dye dianion $1c^{2-}$ display 6π aromaticity in only one of the two rings. To enable a quantitative comparison between the two dianions, contributors in $1c^{2-}$ exhibiting aromaticity in only one ring were assigned a weight of $0.5 \times NRT$ weight, reflecting the partial aromatic character. The calculation method and resulting total NRT weights are also shown in Figures S15 and S16. As a result, the total NRT weight of aromatic resonance contributors was estimated to be 53.7% for $2c^{2-}$, whereas that for $1c^{2-}$ was markedly lower at 19.5%.



Sum of NRT weight of five-membered rings that satisfy Hückel aromaticity: $7.13 \times 1 + 6.21 \times 2 / 2 + 6.15 \times 2 / 2 = 19.49$ (%)

Sum of NRT weight (>2%): 7.13×1 + 6.21×2 + 6.15×2 + 3.91×2 + 3.85×2 + 2.79 ×1 + 2.79 ×1 = **52.95** (%)

Fig. S15. Representative resonance contributors of $1c^{2-}$ obtained from NRT analysis at the ω B97X-D/6-31+G(d) level of theory. Contributors with NRT weights below 2% are omitted for clarity. The number of equivalent degenerate structures due to molecular symmetry is indicated where applicable. Resonance structures are categorized into Type I (at least one five-membered ring exhibits 6π

aromaticity; highlighted in pink) and Type II (nonaromatic). For contributors with aromaticity in only one ring, $0.5 \times NRT$ weight was applied in the calculation of total aromatic contribution. The total NRT weight of aromatic contributors was estimated to be 19.5%.



Fig. S16. Representative resonance contributors of $2c^{2-}$ obtained from NRT analysis at the ω B97X-D/6-31+G(d) level of theory. Contributors with NRT weights below 2% are omitted for clarity. The number of equivalent degenerate structures due to molecular symmetry is indicated where applicable. All dominant resonance contributors are classified as Type I, exhibiting 6π aromaticity in both five-membered rings. The total NRT weight of aromatic contributors was estimated to be 53.7%.

Benchmark of Density Functionals and Basis Sets







Fig. S18. Difference in bond length compared with the crystal structure of 1a (unit A).



Fig. S19. Difference in bond length compared with the crystal structure of 1a (unit B).



Fig. S20. Difference in bond length compared with the crystal structure of $[K^+([2.2.2]cryptand)]_2 1a^{2-}$.

Natural Population Analysis (NPA)

Table S2. NPA charges of 1b and 1b²⁻, and their differences^{[a][b]}

atom	neutral	dianion	difference
C1	0.396	0.349	-0.047
C2	-0.083	-0.261	-0.178
C3	-0.259	-0.168	0.091
C4	-0.130	-0.359	-0.229
S1	0.306	0.174	-0.132
O1	-0.544	-0.716	-0.172
C5	-0.088	-0.015	0.073
C6	-0.218	-0.289	-0.071
C7	-0.205	-0.268	-0.063
C8	-0.241	-0.252	-0.011
C9	-0.241	-0.254	-0.013
C10	-0.229	-0.354	-0.125
sum o	-1.334		
sum of two six-membered rings			-0.420
total			-1.754

[a] Calculated at the ω B97X-D/6-31+G(d) level of theory. [b] Atom labels correspond to those in the accompanying structure.

C9 C11	C7 C3 C4 CE C6 C2 C10 C8	C1	\supset
atom	neutral	dianion	difference
C1	0.006	-0.113	-0.119
C2	-0.238	-0.269	-0.031
C3	-0.049	-0.240	-0.191
C4	-0.225	-0.329	-0.104
C5	-0.240	-0.333	-0.093
C6	-0.052	0.043	0.095
C7	-0.223	-0.286	-0.063
C8	-0.214	-0.286	-0.072
C9	-0.243	-0.261	-0.018
C10	-0.243	-0.258	-0.015
C11	-0.243	-0.369	-0.126
sum o	f two five-mem	bered rings	-1.076
sum o	of two six-mem	nbered rings	-0.398
		total	-1.474

Table S3. NPA charges of 2b and $2b^{2-}$, and their differences^{[a][b]}

[a] Calculated at the ωB97X-D/6-31+G(d) level of theory. [b] Atom labels correspond to those in the accompanying structure.

Cartesian Coordinates of the Optimized Geometries

Table S4. Cartesian coordinates (Å) of the optimized geometry for 1^{2-} calculated at the ω B97X-D/6-31+G(d) level of theory.

С	-1.022516	2.895056	0.00000
С	-1.186267	1.535960	0.00000
С	0.002686	0.742249	0.00000
С	1.186267	1.513955	0.00000
S	0.678894	3.308558	0.00000
Н	-1.795233	3.655731	0.00000
0	2.407031	1.231816	0.00000
С	1.022516	-2.895056	0.00000
С	1.186267	-1.535960	0.00000
С	-0.002686	-0.742249	0.00000
С	-1.186267	-1.513955	0.00000
S	-0.678894	-3.308558	0.00000
Н	1.795233	-3.655731	0.00000
0	-2.407031	-1.231816	0.00000
Н	2.160314	-1.055839	0.00000
Н	-2.160314	1.055839	0.00000

Table S5. Cartesian coordinates (Å) of the optimized geometry for 2^{2-} calculated at the ω B97X-D/6-31+G(d) level of theory.

С	2.944511	0.707941	0.000000
С	1.591992	1.134443	0.00000
С	0.741199	0.000000	0.00000
С	1.591992	-1.134443	0.00000
С	2.944511	-0.707941	0.00000
Н	3.823762	1.354466	0.00000
Н	1.253794	2.170256	0.00000
Н	1.253794	-2.170256	0.00000
Н	3.823762	-1.354466	0.00000
С	-0.741199	0.000000	0.00000
С	-1.591992	1.134443	0.00000
С	-2.944511	0.707941	0.000000
С	-2.944511	-0.707941	0.000000
С	-1.591992	-1.134443	0.000000
Н	-1.253794	2.170256	0.000000
Н	-3.823762	1.354466	0.00000
Н	-3.823762	-1.354466	0.00000
Н	-1.253794	-2.170256	0.00000

Table S6. Cartesian coordinates (Å) of the optimized geometry for $1b^{2-}$ calculated at the ω B97X-D/6-31+G(d) level of theory.

S	-0.689922	3.294792	0.000000
0	-2.379632	1.221219	0.000000
С	2.057619	3.899988	0.000000
С	1.179256	1.517562	0.00000
Н	2.148995	1.031232	0.00000
С	0.013849	0.736197	0.00000
С	1.030253	2.901488	0.00000
С	-1.179256	1.530540	0.00000
С	4.121131	5.894198	0.00000
С	3.440214	3.559924	0.00000
Н	3.724847	2.511782	0.00000
С	1.767826	5.291515	0.00000
Н	0.727901	5.609263	0.000000
С	4.432277	4.527608	0.000000
Н	5.474875	4.210369	0.000000
С	2.770502	6.253206	0.000000
Н	2.489775	7.306561	0.000000
S	0.689922	-3.294792	0.000000
0	2.379632	-1.221219	0.000000
С	-2.057619	-3.899988	0.000000
С	-1.179256	-1.517562	0.000000
Н	-2.148995	-1.031232	0.00000
С	-0.013849	-0.736197	0.00000
С	-1.030253	-2.901488	0.00000
С	1.179256	-1.530540	0.00000
С	-4.121131	-5.894198	0.00000
С	-3.440214	-3.559924	0.00000
Н	-3.724847	-2.511782	0.00000
С	-1.767826	-5.291515	0.00000
Н	-0.727901	-5.609263	0.00000
С	-4.432277	-4.527608	0.00000
Н	-5.474875	-4.210369	0.00000
С	-2.770502	-6.253206	0.00000
Н	-2.489775	-7.306561	0.00000
Н	4.904709	6.649038	0.000000
Η	-4.904709	-6.649038	0.00000

Table S7. Cartesian coordinates (Å) of the optimized geometry for 2^{2-} calculated at the ω B97X-D/6-31+G(d) level of theory.

С	-0.715703	2.921638	0.00000
С	1.558280	4.102365	0.00000
С	1.130650	1.569515	0.00000
Н	2.158927	1.217336	0.00000
С	0.008763	0.735625	0.00000
С	0.715703	2.940934	0.00000
С	-1.137410	1.595533	0.00000
С	3.254120	6.433235	0.00000
С	2.980771	4.016217	0.00000
Н	3.439933	3.031382	0.00000
С	1.039306	5.429616	0.00000
Н	-0.039343	5.565207	0.00000
С	3.793907	5.140583	0.00000
Н	4.876593	5.008047	0.00000
С	1.857980	6.549923	0.00000
Н	1.398768	7.539561	0.00000
С	0.715703	-2.921638	0.00000
С	-1.558280	-4.102365	0.00000
С	-1.130650	-1.569515	0.00000
Н	-2.158927	-1.217336	0.00000
С	-0.008763	-0.735625	0.00000
С	-0.715703	-2.940934	0.00000
С	1.137410	-1.595533	0.00000
С	-3.254120	-6.433235	0.00000
С	-2.980771	-4.016217	0.00000
Н	-3.439933	-3.031382	0.00000
С	-1.039306	-5.429616	0.00000
Н	0.039343	-5.565207	0.00000
С	-3.793907	-5.140583	0.00000
Н	-4.876593	-5.008047	0.00000
С	-1.857980	-6.549923	0.00000
Н	-1.398768	-7.539561	0.00000
Н	3.894691	7.313192	0.00000
Н	-3.894691	-7.313192	0.00000
Н	-1.370837	3.790255	0.00000
Н	-2.171171	1.257721	0.000000
Н	1.370837	-3.790255	0.000000
Н	2.171171	-1.257721	0.00000



Fig. S21. Illustration of parameters for the GIMIC computations of $1b^{2-}$ (left) and $2b^{2-}$ (right).

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