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Competition between n→π* interactions and H-bonding: a way to stabilize aminoxyl anions and to improve electron transfer kinetics

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Contents

1. *Experimental details*

Mass spectra. High resolution mass spectra were recorded with AB Sciex TripleTOF 5600+ instrument using electrospray ionization (DuoSpray ESI).

Voltammetric experiments were performed with Biologic BP-300 potentiostat, in a ALS Co. three-electrode cell of 2 mL with a platinum wire counter electrode (CE) and anhydrous Ag/0.01 M $AgNO_3$ (MeCN) reference electrode (RE). Ferrocene was used as internal standard in each experiment and all measured potentials were converted to the Ag/AgCl,KCl(sat.) reference electrode (in the latter scale, the potential for the $Fc^{0/+}$ redox couple is equal to 0.475 V in acetonitrile). A glassy carbon disk electrode with active surface area of 0.071 cm^2 was used as the working electrode (WE). Hardware ohmic drop compensation was employed. All solutions were thoroughly deaerated by passing an argon flow through the solution prior to the CV experiments and above the solution during the measurements, the supporting electrolyte in all experiments was 0.1 M nBu$_4$NBF$_4$ (Aldrich, purity > 99%), which has been recrystallized from water and dried by heating at 150°C under reduced pressure (0.05 Torr) prior to use. Acetonitrile (82°C / 1 atm) was distilled over P_2O_5 and stored under argon.

Digital simulation of the experimental CV curves was performed using DigiElch 7.0 program.

The ESR spectra were recorded with the X-band Bruker EMX-plus spectrometer for solutions deaerated using a standard freeze-pump-thaw technique (concentrations of radicals were 0.2– 0.4 mM). The ESR spectra of the radicals' solutions were registered at 290 K with 1 mW microwave power and 0.5 G modulation amplitude.

Quantum-chemical calculations were carried out using PBEh-3c [1] approach, including gCP [2] and D3BJ [3,4] corrections implemented in ORCA 5.0.4 quantum chemistry package.[5] A threshold of $1\cdot10^{-8}$ Hartree was used for SCF convergence; thresholds of $1\cdot10^{-6}$ Hartree and $3\cdot10^{-5}$ Hartree $Bohr^{-1}$ on energy and RMS gradient, respectively, were employed in optimization procedures. SMD solvation model [6] was used for geometry optimizations in acetonitrile solution.

Solvents used for synthesis and chromatography were purified prior to experiments according to standard procedures.[7]

Previously described amine (precursor of nitroxide **1**) was prepared according to literature procedure [8]. All other reactants were commercially available and used as recieved.

2. *Synthesis of nitroxide* **1**

A solution of 96 mg of meta-chloroperbenzoic acid (c.a. 70% peracid content, 0.39 mmol) in 1.3 ml of dichloromethane was added to a solution of 95 mg (0.26 mmol) of 2-pivaloyl-4,4'-*tert*-butyldiphenylamine in 6.5 ml of dichloromethane under stirring. The solution turned intensively red. The mixture was kept at room temperature for 30 min, then diluted with 16 ml of hexane and washed with saturated aqueous Na_2CO_3. Organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated. After chromatographic separation on silica gel two fractions were obtained: the targeted nitroxide **1** (48 mg, dark-red amorphous solid, 49%; eluent – hexane/ethyl acetate 12:1) and the starting amine (27 mg).

Characterization of **1**:

HRMS (ESI): m/z 381.2665 ($[M+H]^+$, 381.26652 calc. for $C_{25}H_{35}NO_2^+$)
ESR in hexane: g = 2.00574, a_N = 9.69 G, a_H = 1.99 G (2H), 1.67 G (1H), 0.80 G (4H)

3. *ESI-HRMS of nitroxide* **1**

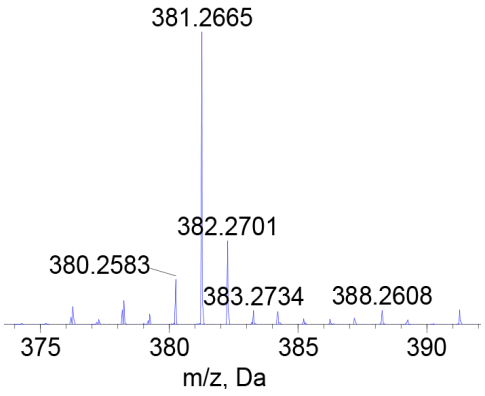


Fig. S1. Molecular ion cluster in the ESI-HRMS spectrum of nitroxide **1**.

4. *ESR spectrum of nitroxide* **1**

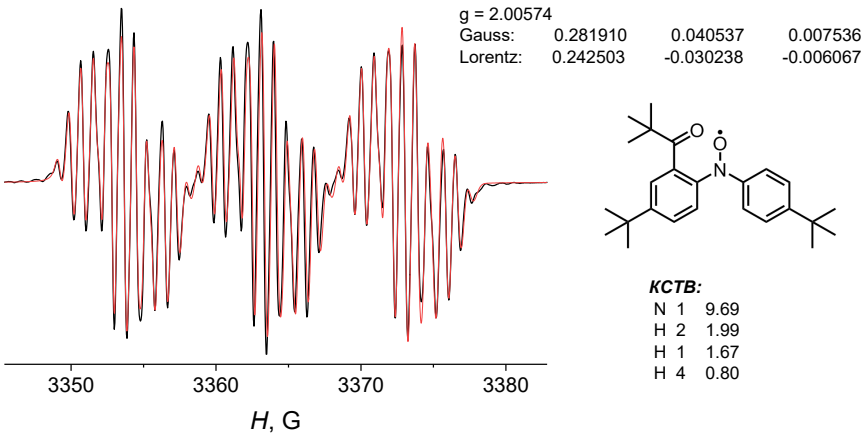


Fig. S2 ESR spectrum of nitroxide **1** in hexane at room temperature

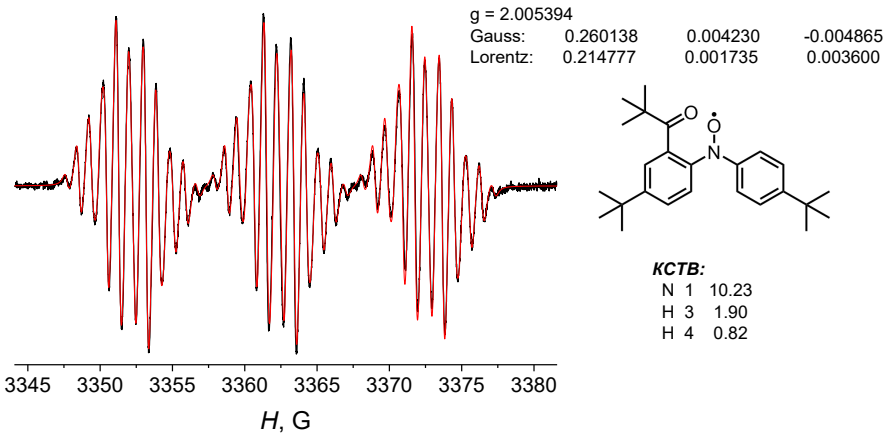


Fig. S3 ESR spectrum of nitroxide **1** in CH_2Cl_2 at room temperature

5. *Cyclic voltammograms of nitroxide* **1**

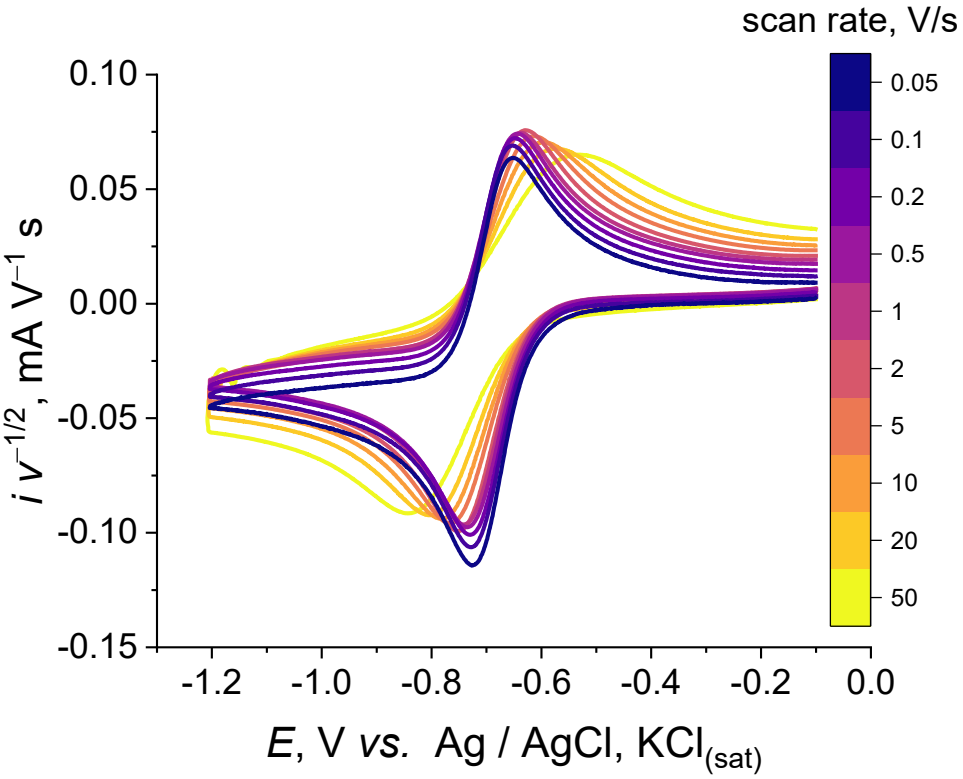


Fig. S4. Reduction of nitroxide **1** (3 mM solution in MeCN, 0.1 M Bu_4NBF_4, glassy carbon electrode) at varying scan rate. Superimposed voltammograms normalized on the square root of scan rate.

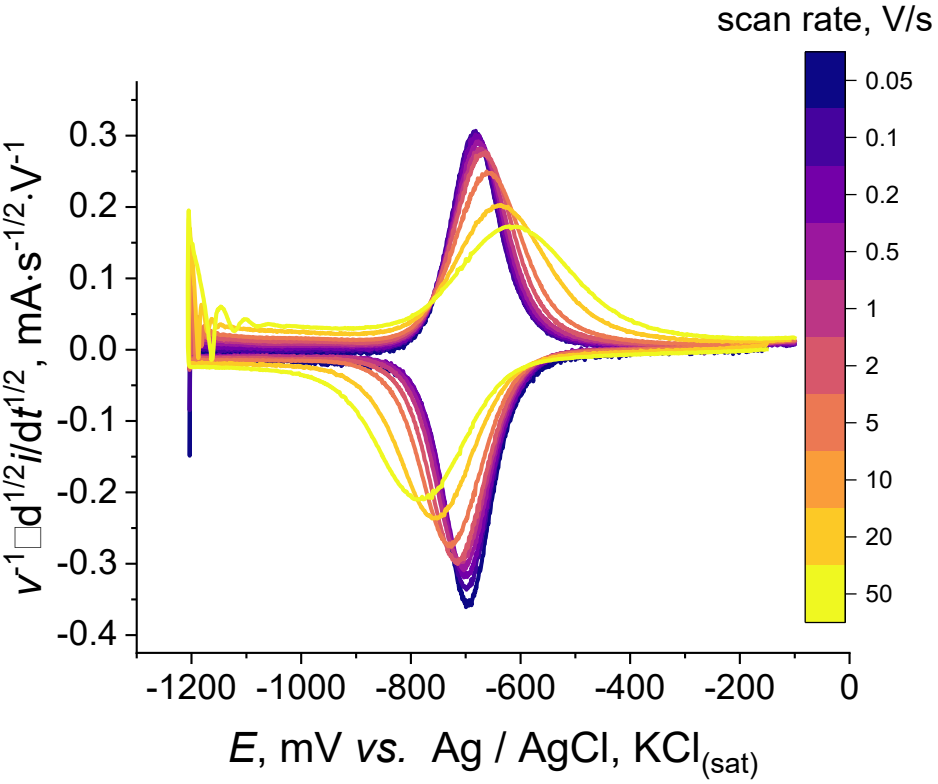


Fig. S5. Reduction of nitroxide **1** (3 mM solution in MeCN, 0.1 M Bu_4NBF_4, glassy carbon electrode) at varying scan rate. Superimposed semi-differential voltammograms.

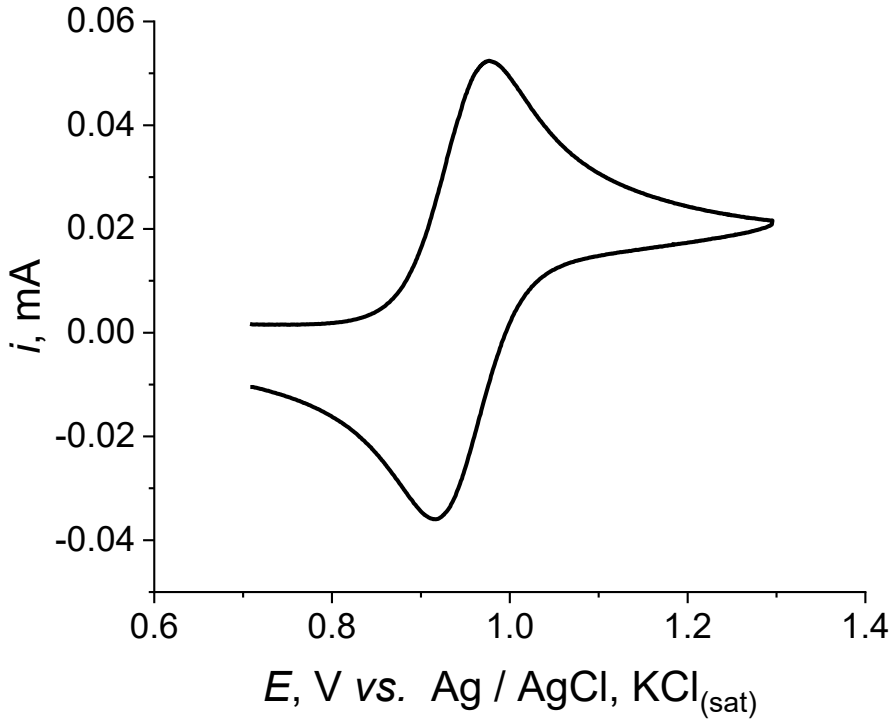


Fig. S6. Oxidation of nitroxide **1** (3 mM solution in MeCN, 0.1 M Bu_4NBF_4, glassy carbon electrode, 0.1 V/s potential scan rate).

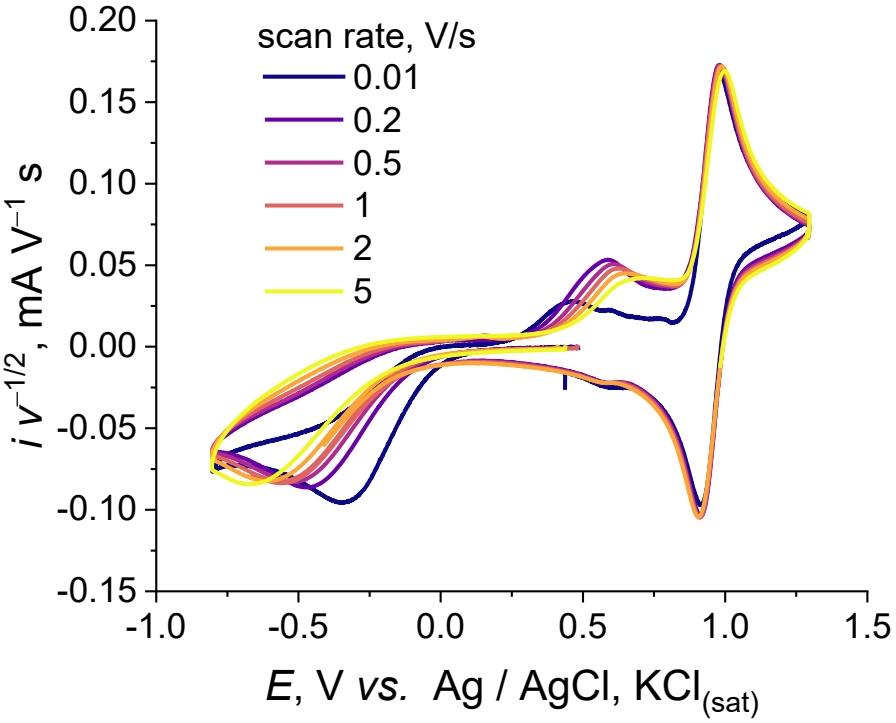


Fig. S7. Voltammogram of nitroxide **1** with acetic acid added (3 mM solution of **1** and 10 mM solution of AcOH in MeCN, 0.1 M Bu_4NBF_4, glassy carbon electrode) at varying scan rate. Superimposed voltammograms normalized on the square root of scan rate.

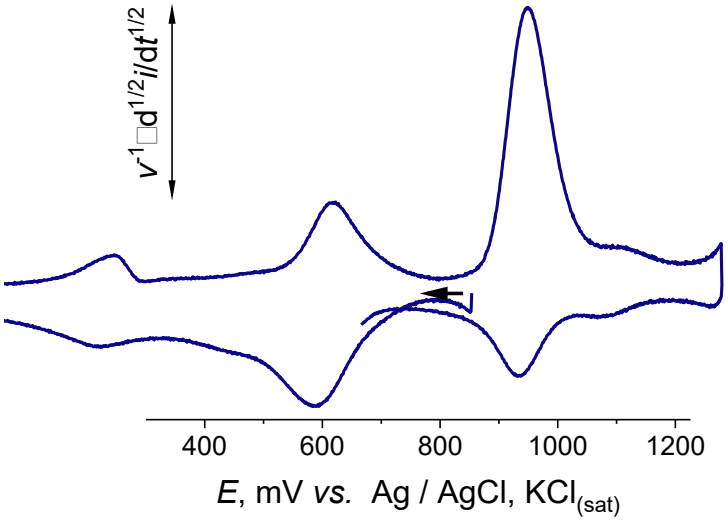


Fig. S8. Semi-differential voltammogram of nitroxide **1** with trifluoroacetic acid added (3 mM solution of **1** and 10 mM solution of CF_3CO_2H in MeCN, 0.1 M Bu_4NBF_4, glassy carbon electrode, 0.1 V/s potential scan rate)

6. Details of CV fitting

For digital simulation, the electrode surface area $S = 0.071$ cm^2, double-layer capacitance C_d and diffusion coefficient of the radical D are required. The diffusion coefficient was determined to be equal $8 \cdot 10^{-6}$ cm^2/s from the limiting value of the semi-integral function I_L [9] (Fig. 7SI):

$$D = \left(\frac{I_L}{FSc^0} \right)^2 = 6.7 \cdot 10^{-6} cm^2 / s$$

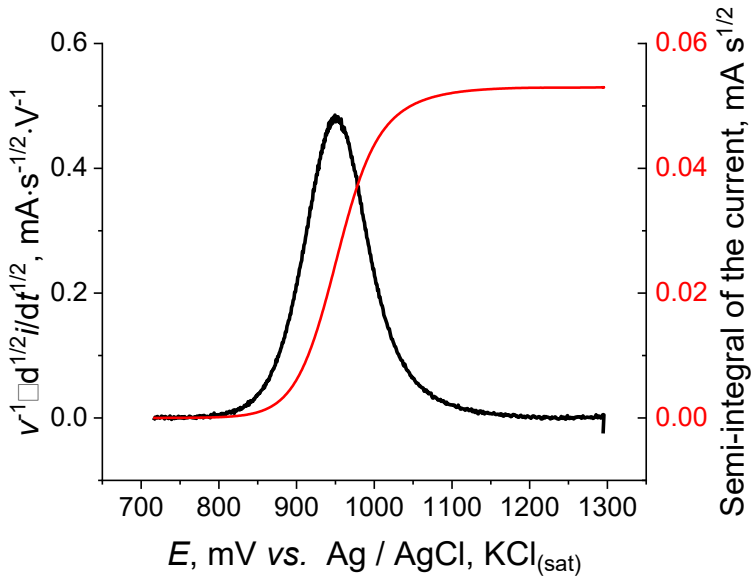


Fig. S9. Semi-integral voltammogram of nitroxide **1** (red) and corresponding semi-differential voltammogram.

Double-layer capacitance $C_d = 1$ μF was determined from the slope of the current vs. potential scan rate linear plot [9] (see Fig. 8SI). The current was measured at the potential $E = -0.43$ V at which no Faradaic processes was observed.

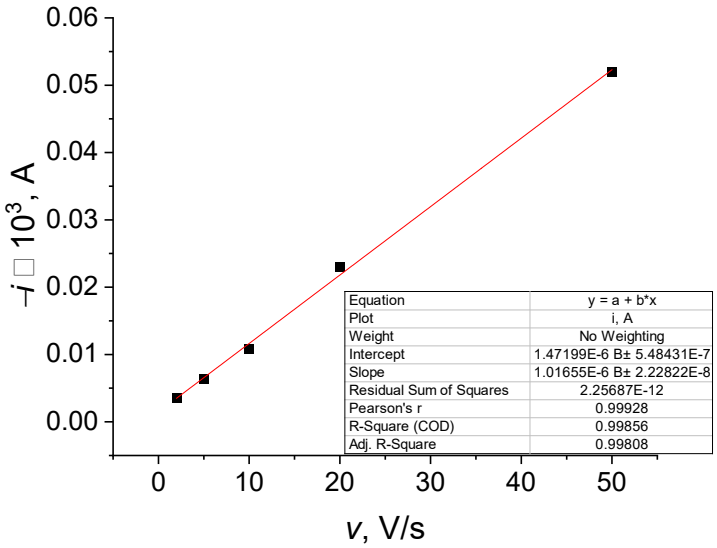


Fig. S10. Double-layer capacitance determination for further use in digital simulation of the CVs

For determination of the standard heterogeneous electron transfer rate constants for both reduction and oxidation processes peak potentials for direct and reverse peaks were determined at various scan rates (Fig. 9SI).

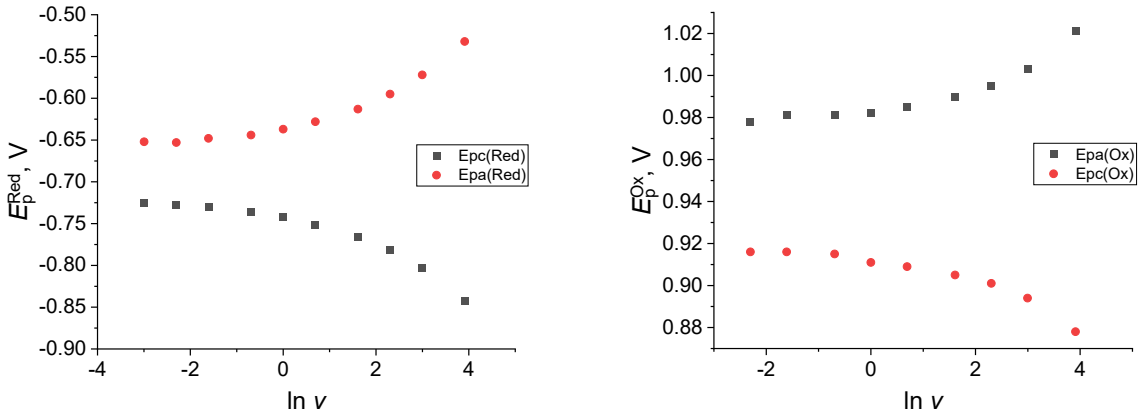


Fig. S11. Cathodic and anodic peak potential dependences on scan rate logarithm for reduction and oxidation processes of nitroxide **1** .

Thus obtained peak-to-peak separations were used for determination of the standard heterogeneous electron transfer rate constants k_s using the following equation [10] (valid for the transfer coefficient α equal to 0.5):

$$\lg k_s\sqrt{\frac{RT}{FvD}} = \underbrace{0.294\left(\frac{F}{RT}\Delta E_{pp} - 2.218\right)^{-1} - 0.0803 - 0.108\left(\frac{F}{RT}\Delta E_{pp} - 2.218\right)}_{f\left(\Delta E_{pp}\right)}$$

$$f\left(\Delta E_{pp}\right) = \lg k_s\sqrt{\frac{RT}{FD}} - \frac{1}{2}\lg v$$

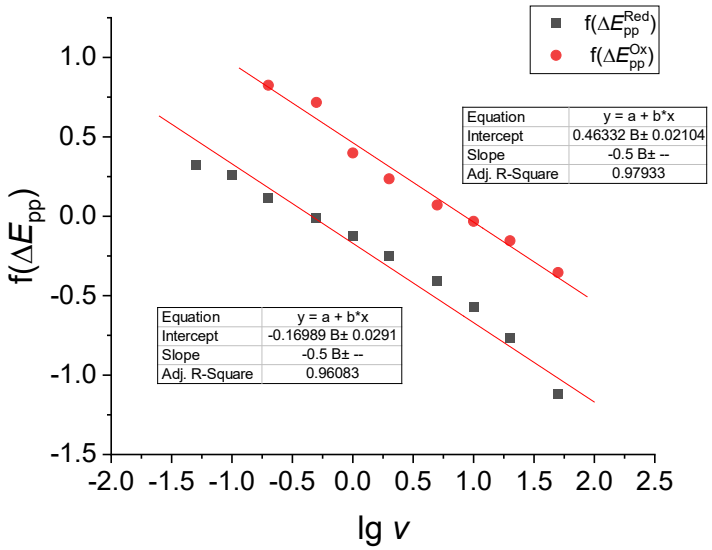


Fig. S12. Determination of the k_s values from the dependences of peak-to-peak separation from logarithm of the scan rate.

Intercept values of the obtained linear dependences yield the k_s values which appeared to be equal 0.01 cm/s for reduction process and 0.05 cm/s for oxidation process of nitroxide **1**. The D, k_s and E^0 values were used to simulate cyclic voltammograms and determine the other parameters describing chemical and electrochemical transformations from Scheme 1SI. The resulting optimized values are given in Table 1SI, the fitting curves superimposed on the experimental CVs are given in Fig. 11SI.

Table S1

EC steps			
Process	E, V	k, cm/s	α
$\mathbf{1^+ \rightleftarrows 1^\bullet}$	0.947	0.04	0.5
$\mathbf{1^\bullet \rightleftarrows 1^-}$	−0.69	0.01	0.5
$\mathbf{1^\bullet \cdots HOAc \rightleftarrows 1H \cdots {}^-OAc}$	0.014	0.009	0.25
$\mathbf{1H^+ \rightleftarrows 1H}$	0.62	0.019	0.6
Chemical steps			
Process	K	k_f	k_b
$\mathbf{1^- + AcOH \rightleftarrows 1H \cdots {}^-OAc}$	$9.5 \cdot 10^{11}$ l mol^{-1}	10^{14} l mol^{-1} s^{-1}	10^5 s^{-1}
$\mathbf{1^\bullet + AcOH \rightleftarrows 1^\bullet \cdots HOAc}$	1.2 l mol^{-1}	10^{12} l mol^{-1} s^{-1}	$8 \cdot 10^{11}$ s^{-1}
$\mathbf{1^\bullet \cdots HOAc \rightleftarrows 1H^+ + {}^-OAc}$	$1 \cdot 10^{-11}$ mol l^{-1}	100 s^{-1}	10^{13} l mol^{-1} s^{-1}
$\mathbf{1H \cdots {}^-OAc \rightleftarrows 1H + {}^-OAc}$	0.17 mol l^{-1}	50 s^{-1}	287 l mol^{-1} s^{-1}

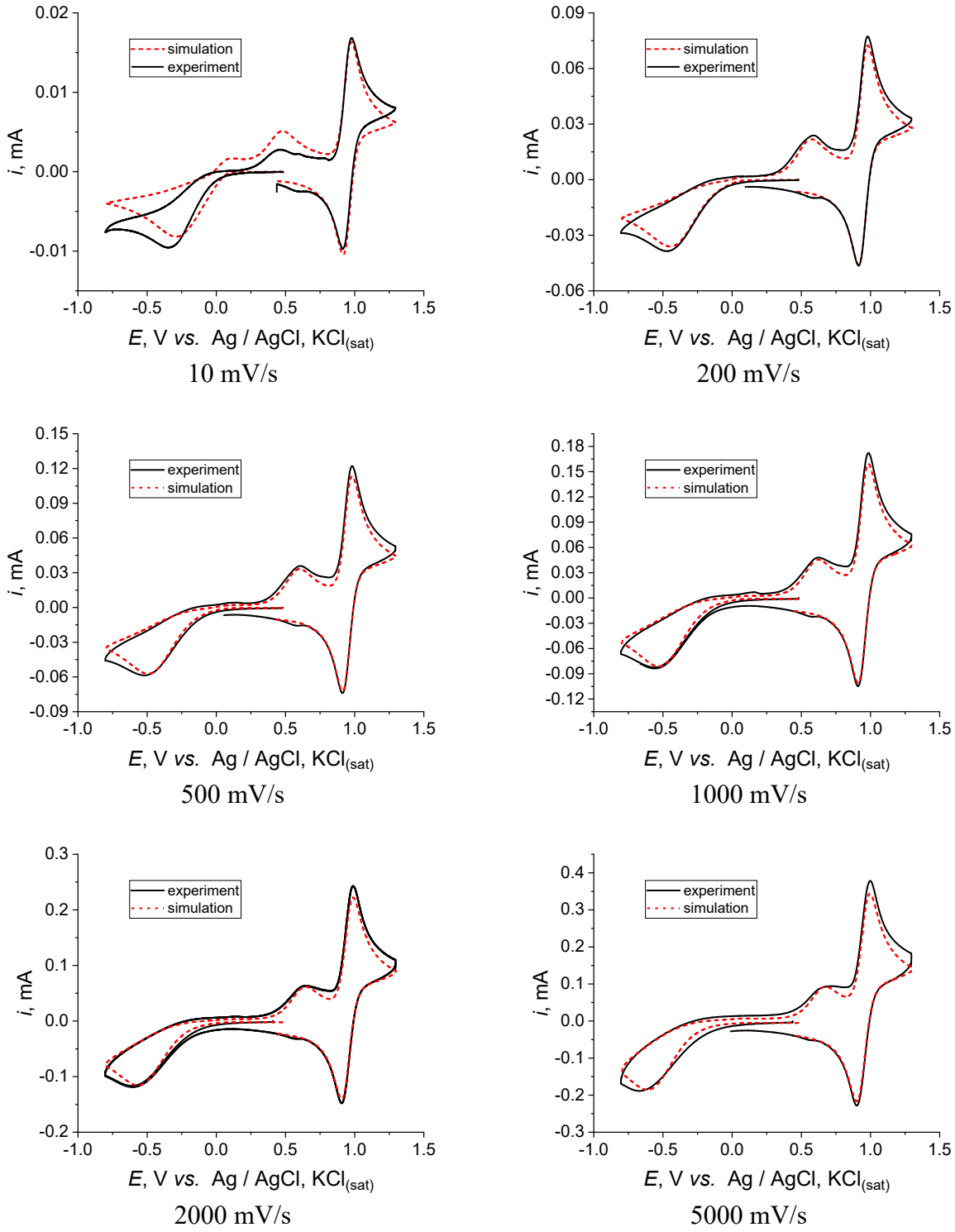
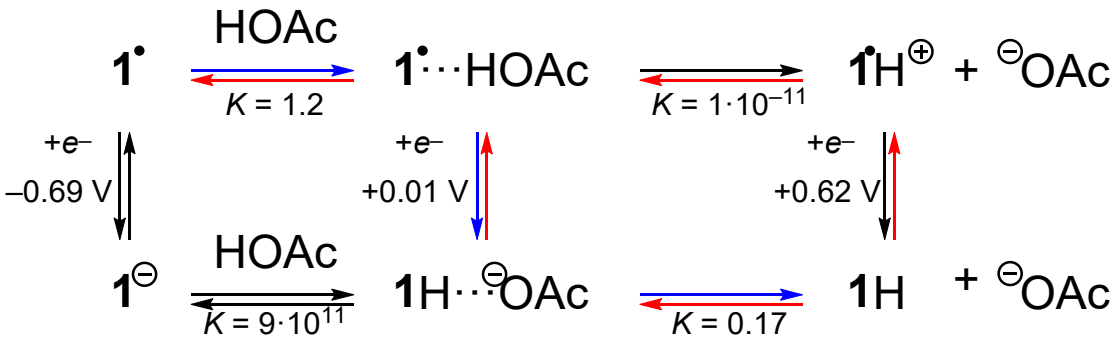


Fig. S13. Comparison of the fitted and experimental CV curves for nitroxide **1** + AcOH solution in MeCN.

Scheme S1



7. DFT-optimized molecular structures and corresponding electronic energies

a. Conformers of nitroxide **1**

Conformer **1a**			Ee = -1175.778321451614Hartree
Element	x, Å	y, Å	z, Å
C	-2.839397000000	-1.357249000000	2.873207000000
C	-3.915788000000	-1.132060000000	2.008838000000
C	-3.612969000000	-0.843305000000	0.680321000000
C	-2.302865000000	-0.766251000000	0.228407000000
C	-1.254092000000	-0.970299000000	1.114435000000
C	-1.528133000000	-1.281659000000	2.443457000000
N	0.096902000000	-0.914201000000	0.691037000000
C	0.582132000000	0.041741000000	-0.221536000000
C	-0.063707000000	1.260650000000	-0.400719000000
C	1.767528000000	-0.218237000000	-0.917643000000
C	2.243055000000	0.736565000000	-1.803201000000
C	1.598639000000	1.956833000000	-2.018278000000
C	0.438043000000	2.197132000000	-1.289737000000
O	0.909788000000	-1.743273000000	1.188506000000
H	-3.019335000000	-1.592249000000	3.915060000000
H	-4.401665000000	-0.678150000000	-0.040433000000
H	-2.114971000000	-0.558248000000	-0.816921000000
C	2.507937000000	-1.530214000000	-0.813625000000
H	3.152835000000	0.517175000000	-2.347682000000
C	2.193775000000	2.963410000000	-2.994746000000
H	-0.097718000000	3.130389000000	-1.391817000000
H	-0.955862000000	1.501264000000	0.160979000000
C	-5.344070000000	-1.221914000000	2.531945000000
O	2.119275000000	-2.469385000000	-1.464768000000
C	3.816443000000	-1.579885000000	-0.020216000000
C	3.966485000000	-2.954143000000	0.634042000000
C	4.963705000000	-1.386594000000	-1.026605000000
C	3.905718000000	-0.486949000000	1.042312000000
H	4.923642000000	-3.008015000000	1.156175000000
H	3.179631000000	-3.138732000000	1.365544000000
H	3.944573000000	-3.760099000000	-0.098967000000
H	5.918599000000	-1.485018000000	-0.506467000000
H	4.938845000000	-2.133369000000	-1.821561000000
H	4.951541000000	-0.397976000000	-1.487786000000

H	4.852778000000	-0.577170000000	1.578101000000
H	3.875096000000	0.514984000000	0.611747000000
H	3.103778000000	-0.565852000000	1.775254000000
H	-0.722098000000	-1.451937000000	3.144458000000
C	-6.375321000000	-0.876015000000	1.458765000000
C	-5.608117000000	-2.651551000000	3.019715000000
C	-5.524862000000	-0.246271000000	3.702152000000
H	-6.630420000000	-2.742267000000	3.393483000000
H	-5.483434000000	-3.375783000000	2.212357000000
H	-4.936675000000	-2.937564000000	3.830804000000
H	-6.550454000000	-0.292655000000	4.074625000000
H	-4.865110000000	-0.478921000000	4.538782000000
H	-5.328375000000	0.782803000000	3.395115000000
H	-7.379688000000	-0.947139000000	1.879689000000
H	-6.252086000000	0.141820000000	1.083513000000
H	-6.334014000000	-1.557200000000	0.606536000000
C	1.319542000000	4.207648000000	-3.145155000000
C	3.571776000000	3.399093000000	-2.479197000000
C	2.347094000000	2.316856000000	-4.376984000000
H	4.019478000000	4.125587000000	-3.161072000000
H	3.496629000000	3.867540000000	-1.495964000000
H	4.263982000000	2.559454000000	-2.395853000000
H	2.772267000000	3.034531000000	-5.081810000000
H	3.007704000000	1.448728000000	-4.360491000000
H	1.382605000000	1.994378000000	-4.773832000000
H	1.779127000000	4.890424000000	-3.861682000000
H	0.322377000000	3.967048000000	-3.518964000000
H	1.207892000000	4.751751000000	-2.205646000000

Conformer **1b**			Ee = -1175.775711695139Hartree
Element	x, Å	y, Å	z, Å
C	-1.929107000000	0.227132000000	2.397603000000
C	-2.548167000000	-0.922853000000	2.896679000000
C	-1.831990000000	-2.115586000000	2.811432000000
C	-0.562148000000	-2.169044000000	2.255626000000
C	0.025424000000	-1.010635000000	1.757833000000
C	-0.665789000000	0.196754000000	1.838533000000
N	1.323987000000	-1.068204000000	1.215298000000
C	1.806491000000	-0.092397000000	0.301261000000
C	2.987904000000	0.566404000000	0.608052000000
C	1.138866000000	0.198522000000	-0.888531000000
C	1.657044000000	1.185964000000	-1.716887000000
C	2.841664000000	1.864426000000	-1.428288000000
C	3.500734000000	1.525890000000	-0.249704000000
O	2.129454000000	-1.957501000000	1.611412000000
H	-2.438159000000	1.181682000000	2.448171000000
H	-2.257354000000	-3.038902000000	3.180047000000
H	-0.037158000000	-3.113332000000	2.208724000000
C	-0.138423000000	-0.463535000000	-1.347798000000
H	1.122702000000	1.420878000000	-2.629726000000
C	3.348491000000	2.935886000000	-2.386544000000

H	4.422488000000	2.016542000000	0.029483000000
H	3.503335000000	0.339344000000	1.532161000000
C	-3.945395000000	-0.832081000000	3.498715000000
O	-1.178499000000	0.133291000000	-1.216040000000
C	-0.050637000000	-1.782308000000	-2.108362000000
C	-1.434436000000	-2.418544000000	-2.208818000000
C	0.456808000000	-1.433219000000	-3.519001000000
C	0.923419000000	-2.773108000000	-1.471730000000
H	-1.364531000000	-3.359044000000	-2.758323000000
H	-1.846813000000	-2.643100000000	-1.223341000000
H	-2.145836000000	-1.782111000000	-2.734274000000
H	0.477159000000	-2.342289000000	-4.122764000000
H	-0.195168000000	-0.715864000000	-4.020422000000
H	1.468284000000	-1.025344000000	-3.503986000000
H	0.986123000000	-3.659038000000	-2.105961000000
H	1.933429000000	-2.372511000000	-1.381314000000
H	0.588790000000	-3.103023000000	-0.488189000000
H	-0.221480000000	1.116575000000	1.482770000000
C	-4.432492000000	-2.175214000000	4.039057000000
C	-3.937421000000	0.176283000000	4.654305000000
C	-4.928188000000	-0.359864000000	2.419709000000
H	-4.930601000000	0.246322000000	5.103182000000
H	-3.239691000000	-0.123702000000	5.438722000000
H	-3.658791000000	1.177986000000	4.324634000000
H	-5.935851000000	-0.275386000000	2.832906000000
H	-4.656804000000	0.617245000000	2.016789000000
H	-4.968726000000	-1.063813000000	1.585988000000
H	-5.429430000000	-2.057040000000	4.467207000000
H	-4.505592000000	-2.935174000000	3.258568000000
H	-3.784107000000	-2.562222000000	4.827603000000
C	4.690244000000	3.515539000000	-1.942583000000
C	3.522536000000	2.333866000000	-3.786713000000
C	2.321495000000	4.073492000000	-2.444819000000
H	3.899439000000	3.091017000000	-4.477223000000
H	4.234019000000	1.505793000000	-3.778647000000
H	2.583096000000	1.960897000000	-4.197111000000
H	2.659645000000	4.856403000000	-3.127275000000
H	1.348978000000	3.727415000000	-2.798127000000
H	2.177810000000	4.528275000000	-1.462859000000
H	5.023609000000	4.263019000000	-2.664403000000
H	4.626359000000	4.010497000000	-0.971647000000
H	5.468954000000	2.752654000000	-1.881065000000

Conformer **1c**			Ee = -1175.777324892390Hartree
Element	x, Å	y, Å	z, Å
C	-1.044065000000	-0.064346000000	2.663482000000
C	-1.731437000000	-1.126218000000	3.256859000000
C	-1.249682000000	-2.410554000000	3.004657000000
C	-0.145157000000	-2.635264000000	2.197958000000
C	0.513528000000	-1.560598000000	1.610815000000
C	0.061951000000	-0.265632000000	1.856833000000

N	1.636707000000	-1.791761000000	0.798405000000
C	2.051129000000	-0.867042000000	-0.199129000000
C	3.353333000000	-0.401063000000	-0.157711000000
C	1.185059000000	-0.439572000000	-1.212634000000
C	1.671412000000	0.450306000000	-2.161566000000
C	2.985730000000	0.921568000000	-2.150226000000
C	3.815114000000	0.479251000000	-1.125347000000
O	2.329499000000	-2.834366000000	0.962544000000
H	-1.369362000000	0.954980000000	2.831641000000
H	-1.740225000000	-3.273317000000	3.433908000000
H	0.191343000000	-3.647137000000	2.018905000000
C	-0.169869000000	-1.068397000000	-1.379362000000
H	1.015841000000	0.763169000000	-2.963196000000
C	3.450983000000	1.878228000000	-3.242787000000
H	4.839833000000	0.817053000000	-1.057573000000
H	4.013965000000	-0.720881000000	0.637721000000
C	-2.959065000000	-0.853299000000	4.117568000000
O	-0.241564000000	-2.273667000000	-1.321294000000
C	-1.420445000000	-0.227173000000	-1.655189000000
C	-1.703446000000	-0.290320000000	-3.164617000000
C	-2.596252000000	-0.867390000000	-0.908542000000
C	-1.292786000000	1.231212000000	-1.214499000000
H	-2.629923000000	0.243900000000	-3.384275000000
H	-0.912049000000	0.170631000000	-3.757598000000
H	-1.823257000000	-1.319209000000	-3.506570000000
H	-3.505893000000	-0.299977000000	-1.111993000000
H	-2.769029000000	-1.896092000000	-1.220913000000
H	-2.438598000000	-0.862798000000	0.172296000000
H	-2.256945000000	1.727828000000	-1.338343000000
H	-1.014835000000	1.320458000000	-0.163637000000
H	-0.569101000000	1.794770000000	-1.801602000000
H	0.574231000000	0.590174000000	1.437150000000
C	-3.534625000000	-2.131376000000	4.726343000000
C	-2.584768000000	0.095761000000	5.262844000000
C	-4.041412000000	-0.199507000000	3.249576000000
H	-3.458383000000	0.299337000000	5.886023000000
H	-1.815203000000	-0.340913000000	5.902194000000
H	-2.214195000000	1.055576000000	4.900484000000
H	-4.932102000000	0.011619000000	3.845777000000
H	-3.705729000000	0.744484000000	2.817123000000
H	-4.341459000000	-0.853621000000	2.428003000000
H	-4.405219000000	-1.885992000000	5.336914000000
H	-3.862355000000	-2.840925000000	3.964307000000
H	-2.815696000000	-2.638140000000	5.373405000000
C	4.917006000000	2.274276000000	-3.073585000000
C	3.291102000000	1.202652000000	-4.611068000000
C	2.595867000000	3.150241000000	-3.199859000000
H	3.617124000000	1.878222000000	-5.404774000000
H	3.895271000000	0.295912000000	-4.676258000000
H	2.255288000000	0.930878000000	-4.819477000000
H	2.916142000000	3.846503000000	-3.977933000000
H	1.537248000000	2.942247000000	-3.365474000000

H	2.689246000000	3.660891000000	-2.239259000000
H	5.206324000000	2.955945000000	-3.874887000000
H	5.101101000000	2.787834000000	-2.128155000000
H	5.582759000000	1.410638000000	-3.124395000000

b. Conformers of anion $\mathbf{1}^-$

Conformer $\mathbf{1a}^-$			Ee = -1175.890156398210Hartree
Element	x, Å	y, Å	z, Å
C	-2.750701000000	-1.835103000000	2.571486000000
C	-3.887929000000	-1.194662000000	2.069227000000
C	-3.690404000000	-0.399359000000	0.943074000000
C	-2.444118000000	-0.228881000000	0.356408000000
C	-1.303432000000	-0.851141000000	0.888271000000
C	-1.498529000000	-1.684408000000	2.007227000000
N	-0.040242000000	-0.736765000000	0.364512000000
C	0.455579000000	0.222697000000	-0.475416000000
C	-0.098139000000	1.478506000000	-0.757407000000
C	1.691546000000	-0.106688000000	-1.060022000000
C	2.268968000000	0.755444000000	-1.975076000000
C	1.714073000000	1.998909000000	-2.299405000000
C	0.528734000000	2.336198000000	-1.650907000000
O	0.853053000000	-1.700967000000	0.673446000000
H	-2.835558000000	-2.479304000000	3.439763000000
H	-4.527490000000	0.103842000000	0.476454000000
H	-2.387899000000	0.361797000000	-0.545974000000
C	2.333454000000	-1.436814000000	-0.739307000000
H	3.198282000000	0.455106000000	-2.446814000000
C	2.416390000000	2.914372000000	-3.296732000000
H	0.060591000000	3.295445000000	-1.829040000000
H	-1.002819000000	1.813950000000	-0.272072000000
C	-5.244466000000	-1.393989000000	2.735601000000
O	2.285379000000	-2.328167000000	-1.579795000000
C	3.491613000000	-1.435609000000	0.287847000000
C	3.589492000000	-2.797250000000	0.974477000000
C	4.784568000000	-1.208578000000	-0.512356000000
C	3.388203000000	-0.338418000000	1.343096000000
H	4.478057000000	-2.836501000000	1.610329000000
H	2.720437000000	-2.990253000000	1.602654000000
H	3.671791000000	-3.606703000000	0.248291000000
H	5.649559000000	-1.228042000000	0.155352000000
H	4.931919000000	-1.980969000000	-1.268551000000
H	4.793923000000	-0.239863000000	-1.016945000000
H	4.264630000000	-0.369430000000	1.996160000000
H	3.356804000000	0.659162000000	0.899514000000
H	2.500010000000	-0.462749000000	1.959685000000
H	-0.653724000000	-2.208602000000	2.429326000000
C	-6.361549000000	-0.649664000000	2.005450000000
C	-5.596447000000	-2.887254000000	2.749589000000
C	-5.187301000000	-0.876756000000	4.178614000000
H	-6.571715000000	-3.049526000000	3.215173000000

H	-5.642786000000	-3.290917000000	1.736147000000
H	-4.868066000000	-3.476083000000	3.309417000000
H	-6.145618000000	-1.026991000000	4.682084000000
H	-4.426128000000	-1.392416000000	4.766744000000
H	-4.961331000000	0.191290000000	4.207668000000
H	-7.311579000000	-0.817239000000	2.516259000000
H	-6.192147000000	0.428812000000	1.981723000000
H	-6.482796000000	-0.993399000000	0.975985000000
C	1.636963000000	4.206606000000	-3.537059000000
C	3.805976000000	3.285130000000	-2.762314000000
C	2.572986000000	2.194245000000	-4.642040000000
H	4.328222000000	3.939329000000	-3.465061000000
H	3.735488000000	3.811531000000	-1.808091000000
H	4.432181000000	2.404678000000	-2.608187000000
H	3.084230000000	2.834886000000	-5.364955000000
H	3.157593000000	1.276952000000	-4.552160000000
H	1.601979000000	1.928566000000	-5.065163000000
H	2.161244000000	4.825997000000	-4.267524000000
H	0.636963000000	4.016200000000	-3.931987000000
H	1.532023000000	4.799811000000	-2.626693000000

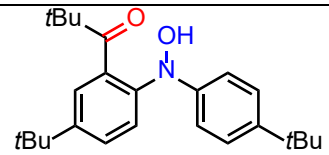
Conformer **1b**$^{-}$			Ee = -1175.878515074843Hartree
Element	x, Å	y, Å	z, Å
C	-2.075328000000	0.164670000000	2.087574000000
C	-2.619682000000	-0.929707000000	2.773969000000
C	-1.799880000000	-2.051146000000	2.871043000000
C	-0.531780000000	-2.102639000000	2.306961000000
C	-0.016724000000	-1.016703000000	1.574468000000
C	-0.822427000000	0.141066000000	1.510963000000
N	1.243456000000	-1.113800000000	1.046111000000
C	1.797188000000	-0.171204000000	0.201711000000
C	3.095017000000	0.303267000000	0.429793000000
C	1.122622000000	0.296445000000	-0.938671000000
C	1.660584000000	1.342540000000	-1.683479000000
C	2.916299000000	1.883762000000	-1.413146000000
C	3.627015000000	1.311851000000	-0.353537000000
O	2.065577000000	-2.056432000000	1.517548000000
H	-2.644008000000	1.085261000000	2.011277000000
H	-2.140026000000	-2.929774000000	3.405773000000
H	0.074186000000	-2.989870000000	2.418119000000
C	-0.115128000000	-0.344394000000	-1.472126000000
H	1.099448000000	1.697681000000	-2.540935000000
C	3.463725000000	3.015111000000	-2.278493000000
H	4.622948000000	1.662428000000	-0.115475000000
H	3.668349000000	-0.104593000000	1.250982000000
C	-4.010749000000	-0.835515000000	3.389974000000
O	-1.117777000000	0.315755000000	-1.643053000000
C	-0.066338000000	-1.791485000000	-1.999030000000
C	-1.219498000000	-2.597128000000	-1.396949000000
C	-0.279424000000	-1.670668000000	-3.517806000000
C	1.254413000000	-2.524479000000	-1.766691000000

H	-1.250421000000	-3.591663000000	-1.846941000000
H	-1.102990000000	-2.726881000000	-0.319892000000
H	-2.183238000000	-2.120536000000	-1.578313000000
H	-0.266331000000	-2.663679000000	-3.971588000000
H	-1.234945000000	-1.205283000000	-3.759127000000
H	0.512618000000	-1.083702000000	-3.989230000000
H	1.207775000000	-3.493714000000	-2.269082000000
H	2.098713000000	-1.982717000000	-2.197334000000
H	1.475624000000	-2.711517000000	-0.715808000000
H	-0.466269000000	1.035767000000	1.018831000000
C	-4.456372000000	-2.158511000000	4.010819000000
C	-4.013840000000	0.236970000000	4.486431000000
C	-5.033258000000	-0.447407000000	2.313446000000
H	-5.004062000000	0.329189000000	4.939868000000
H	-3.307281000000	-0.009587000000	5.281790000000
H	-3.741620000000	1.218338000000	4.093339000000
H	-6.035551000000	-0.369220000000	2.742294000000
H	-4.800021000000	0.515899000000	1.857273000000
H	-5.071162000000	-1.191154000000	1.514425000000
H	-5.463344000000	-2.054983000000	4.420387000000
H	-4.486633000000	-2.966844000000	3.277038000000
H	-3.806703000000	-2.474109000000	4.829810000000
C	4.818908000000	3.516095000000	-1.781085000000
C	3.630433000000	2.524808000000	-3.722707000000
C	2.482718000000	4.194244000000	-2.260232000000
H	4.026556000000	3.321733000000	-4.356663000000
H	4.321217000000	1.680888000000	-3.778070000000
H	2.680996000000	2.206090000000	-4.156320000000
H	2.858737000000	5.016403000000	-2.874022000000
H	1.503549000000	3.917440000000	-2.653503000000
H	2.339067000000	4.576344000000	-1.247454000000
H	5.160484000000	4.341235000000	-2.409197000000
H	4.767288000000	3.888197000000	-0.755857000000
H	5.587297000000	2.741572000000	-1.820207000000

Conformer **1c**$^{-}$		Ee = -1175.874754294025Hartree	
Element	x, Å	y, Å	z, Å
C	-1.248866000000	-0.109633000000	2.593324000000
C	-1.766433000000	-1.199506000000	3.305178000000
C	-1.011911000000	-2.369400000000	3.268000000000
C	0.168923000000	-2.470723000000	2.542642000000
C	0.633628000000	-1.398035000000	1.774859000000
C	-0.085514000000	-0.195613000000	1.855146000000
N	1.814819000000	-1.524640000000	1.067744000000
C	2.133993000000	-0.788996000000	-0.032250000000
C	3.505005000000	-0.568407000000	-0.295193000000
C	1.201016000000	-0.255866000000	-0.978599000000
C	1.681249000000	0.571610000000	-1.994066000000
C	3.027007000000	0.858698000000	-2.203176000000
C	3.926359000000	0.237840000000	-1.331444000000
O	2.725794000000	-2.366580000000	1.565853000000

H	-1.761431000000	0.845623000000	2.622483000000
H	-1.335208000000	-3.244180000000	3.818256000000
H	0.732591000000	-3.392731000000	2.554841000000
C	-0.183546000000	-0.798852000000	-1.116754000000
H	0.972256000000	0.967072000000	-2.708326000000
C	3.450325000000	1.749913000000	-3.367024000000
H	4.992890000000	0.382831000000	-1.451454000000
H	4.229662000000	-1.028808000000	0.359583000000
C	-3.080275000000	-1.062411000000	4.065465000000
O	-0.372196000000	-1.984776000000	-0.940990000000
C	-1.379000000000	0.075780000000	-1.557093000000
C	-1.535070000000	-0.017250000000	-3.084114000000
C	-2.652500000000	-0.509515000000	-0.933572000000
C	-1.274663000000	1.540485000000	-1.127402000000
H	-2.455581000000	0.487017000000	-3.386586000000
H	-0.717707000000	0.450720000000	-3.632509000000
H	-1.604850000000	-1.055566000000	-3.412632000000
H	-3.512141000000	0.096200000000	-1.227543000000
H	-2.838771000000	-1.530716000000	-1.262365000000
H	-2.606970000000	-0.508924000000	0.156741000000
H	-2.190214000000	2.063403000000	-1.411223000000
H	-1.172301000000	1.637629000000	-0.045817000000
H	-0.446311000000	2.075235000000	-1.589034000000
H	0.277815000000	0.689782000000	1.349754000000
C	-3.490857000000	-2.367575000000	4.745371000000
C	-2.945774000000	0.021100000000	5.142293000000
C	-4.194363000000	-0.660293000000	3.088881000000
H	-3.884327000000	0.138864000000	5.689202000000
H	-2.168999000000	-0.232664000000	5.866928000000
H	-2.694610000000	0.993125000000	4.714107000000
H	-5.145237000000	-0.546990000000	3.615452000000
H	-3.979962000000	0.288576000000	2.594780000000
H	-4.332230000000	-1.416692000000	2.313202000000
H	-4.441898000000	-2.232633000000	5.264191000000
H	-3.624539000000	-3.178632000000	4.026782000000
H	-2.759587000000	-2.694483000000	5.487136000000
C	4.959301000000	1.993864000000	-3.377358000000
C	3.061446000000	1.088201000000	-4.695622000000
C	2.747954000000	3.110024000000	-3.264569000000
H	3.360227000000	1.711758000000	-5.542287000000
H	3.545780000000	0.116393000000	-4.812579000000
H	1.983589000000	0.931991000000	-4.772586000000
H	3.035610000000	3.757078000000	-4.096873000000
H	1.661238000000	3.011695000000	-3.290293000000
H	3.013061000000	3.622323000000	-2.337472000000
H	5.224624000000	2.647556000000	-4.210551000000
H	5.301007000000	2.479667000000	-2.460870000000
H	5.526681000000	1.069034000000	-3.497955000000

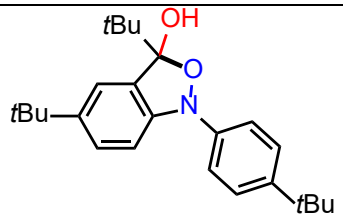
c. *Isomers of* **1H**



Ee = -1176.387323079895Hartree

Element	x, Å	y, Å	z, Å
C	-2.551731000000	-1.309115000000	3.069492000000
C	-3.734758000000	-1.230646000000	2.333942000000
C	-3.606004000000	-1.132083000000	0.949384000000
C	-2.364875000000	-1.110633000000	0.330978000000
C	-1.196464000000	-1.155581000000	1.086834000000
C	-1.302294000000	-1.267014000000	2.471363000000
N	0.046969000000	-1.145054000000	0.427792000000
C	0.456422000000	-0.075366000000	-0.384633000000
C	-0.274361000000	1.103415000000	-0.478416000000
C	1.646177000000	-0.181662000000	-1.120525000000
C	2.053151000000	0.877618000000	-1.917788000000
C	1.313476000000	2.054660000000	-2.046920000000
C	0.139630000000	2.136557000000	-1.308231000000
O	1.089529000000	-1.624674000000	1.204448000000
H	-2.591711000000	-1.398820000000	4.148327000000
H	-4.482896000000	-1.084915000000	0.317908000000
H	-2.308087000000	-1.056314000000	-0.749232000000
C	2.432868000000	-1.462091000000	-1.154368000000
H	2.974773000000	0.773887000000	-2.477715000000
C	1.818594000000	3.175679000000	-2.947913000000
H	-0.474956000000	3.025577000000	-1.346170000000
H	-1.179434000000	1.233518000000	0.098704000000
C	-5.081998000000	-1.262165000000	3.047416000000
O	1.916910000000	-2.445896000000	-1.631596000000
C	3.883510000000	-1.491992000000	-0.659142000000
C	4.120741000000	-2.783633000000	0.129112000000
C	4.793048000000	-1.506365000000	-1.896946000000
C	4.235255000000	-0.295521000000	0.222884000000
H	5.177035000000	-2.859460000000	0.393038000000
H	3.554424000000	-2.800419000000	1.061362000000
H	3.858927000000	-3.670484000000	-0.446616000000
H	5.837001000000	-1.549716000000	-1.579901000000
H	4.600996000000	-2.375156000000	-2.528113000000
H	4.676528000000	-0.611835000000	-2.511088000000
H	5.243408000000	-0.422700000000	0.622033000000
H	4.223112000000	0.646122000000	-0.326001000000
H	3.553463000000	-0.201957000000	1.068870000000
H	-0.418876000000	-1.324650000000	3.091610000000
H	1.126358000000	-2.574832000000	1.019343000000
C	-6.253986000000	-1.120223000000	2.077968000000
C	-5.231061000000	-2.593398000000	3.795558000000
C	-5.152065000000	-0.107726000000	4.054549000000
H	-6.115668000000	-0.109663000000	4.568896000000
H	-4.376071000000	-0.181990000000	4.817429000000

H	-5.042173000000	0.858945000000	3.559078000000
H	-6.193015000000	-2.634839000000	4.311631000000
H	-5.185270000000	-3.441515000000	3.109436000000
H	-4.451856000000	-2.730406000000	4.547505000000
H	-7.192206000000	-1.127576000000	2.635634000000
H	-6.216262000000	-0.182847000000	1.519428000000
H	-6.299458000000	-1.940028000000	1.358251000000
C	0.855059000000	4.360722000000	-2.982600000000
C	3.173969000000	3.669045000000	-2.426060000000
C	1.984584000000	2.652716000000	-4.380086000000
H	3.556373000000	4.473332000000	-3.058801000000
H	3.088733000000	4.058144000000	-1.409409000000
H	3.923971000000	2.876107000000	-2.417431000000
H	2.343591000000	3.449618000000	-5.035015000000
H	2.703111000000	1.833629000000	-4.441366000000
H	1.035519000000	2.294528000000	-4.783507000000
H	1.253312000000	5.138696000000	-3.636412000000
H	-0.126099000000	4.080932000000	-3.371362000000
H	0.713118000000	4.807502000000	-1.996836000000

	Ee = -1176.398345590653Hartree

Element	x, Å	y, Å	z, Å
C	-2.722411000000	-1.490069000000	2.821570000000
C	-3.664068000000	-1.389094000000	1.790931000000
C	-3.255516000000	-0.757435000000	0.621142000000
C	-1.968153000000	-0.251571000000	0.472810000000
C	-1.056762000000	-0.345448000000	1.513951000000
C	-1.447863000000	-0.969776000000	2.696821000000
N	0.265676000000	0.172920000000	1.440844000000
C	0.622491000000	1.004657000000	0.377604000000
C	0.087641000000	2.238167000000	0.051579000000
C	1.630888000000	0.437083000000	-0.380263000000
C	2.092174000000	1.077196000000	-1.514774000000
C	1.580829000000	2.327222000000	-1.877665000000
C	0.584988000000	2.885564000000	-1.072572000000
O	1.217929000000	-0.873308000000	1.442443000000
H	-2.989999000000	-1.972678000000	3.753613000000
H	-3.935269000000	-0.654108000000	-0.213464000000
H	-1.696571000000	0.220424000000	-0.462671000000
C	1.939624000000	-0.921386000000	0.200396000000
H	2.844856000000	0.608109000000	-2.134017000000
C	2.111908000000	3.017539000000	-3.131053000000
H	0.165848000000	3.851465000000	-1.318750000000
H	-0.699000000000	2.687274000000	0.643962000000
C	-5.067750000000	-1.953000000000	1.982233000000

O	1.485332000000	-1.946050000000	-0.617593000000
C	3.411916000000	-1.223702000000	0.577690000000
C	3.482503000000	-2.523134000000	1.390701000000
C	4.277982000000	-1.394590000000	-0.673053000000
C	3.987034000000	-0.079017000000	1.412085000000
H	4.524977000000	-2.740598000000	1.632160000000
H	2.940696000000	-2.456064000000	2.334359000000
H	3.092725000000	-3.377613000000	0.836419000000
H	5.292410000000	-1.662680000000	-0.371720000000
H	3.910645000000	-2.182356000000	-1.329362000000
H	4.358380000000	-0.475428000000	-1.253557000000
H	5.012428000000	-0.316994000000	1.701708000000
H	4.020356000000	0.857502000000	0.851889000000
H	3.421386000000	0.095767000000	2.327494000000
H	-0.751765000000	-1.044447000000	3.523008000000
H	0.644010000000	-1.693376000000	-1.018880000000
C	-5.949203000000	-1.734298000000	0.753996000000
C	-4.977785000000	-3.459916000000	2.249814000000
C	-5.732500000000	-1.265541000000	3.181547000000
H	-5.976828000000	-3.879786000000	2.386785000000
H	-4.508133000000	-3.985865000000	1.416298000000
H	-4.404866000000	-3.683844000000	3.151031000000
H	-6.742683000000	-1.653778000000	3.330460000000
H	-5.180675000000	-1.432647000000	4.107641000000
H	-5.810692000000	-0.187174000000	3.029168000000
H	-6.941092000000	-2.152781000000	0.934264000000
H	-6.081859000000	-0.675132000000	0.524918000000
H	-5.548992000000	-2.224954000000	-0.135397000000
C	1.470292000000	4.386478000000	-3.349878000000
C	3.628247000000	3.212020000000	-3.011581000000
C	1.809797000000	2.142610000000	-4.354403000000
H	4.016888000000	3.717188000000	-3.898697000000
H	3.883675000000	3.823394000000	-2.143691000000
H	4.161029000000	2.264072000000	-2.918540000000
H	2.183242000000	2.618240000000	-5.264164000000
H	2.280507000000	1.160700000000	-4.282876000000
H	0.735642000000	1.989187000000	-4.476550000000
H	1.880343000000	4.846059000000	-4.251054000000
H	0.389353000000	4.318034000000	-3.485921000000
H	1.663773000000	5.070768000000	-2.521184000000

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