Supplementary Data:

Pyridine-Substituted Nitronyl Nitroxide Biradicals: A Triplet (S = 1) Ground State Lasting out *N*-Methylation

Kenichi Hayakawa,[a] Daisuke Shiomi,[*a,b] Tomoaki Ise,[a,b] Kazunobu Sato,[a] and Takeji Takui[*a]

[a] Departments of Materials Science and Chemistry, Graduate School of Science, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan, and [b] PRESTO, Japan Science and Technology Agency (JST), Honcho Kawaguchi, Saitama 332-0012, Japan

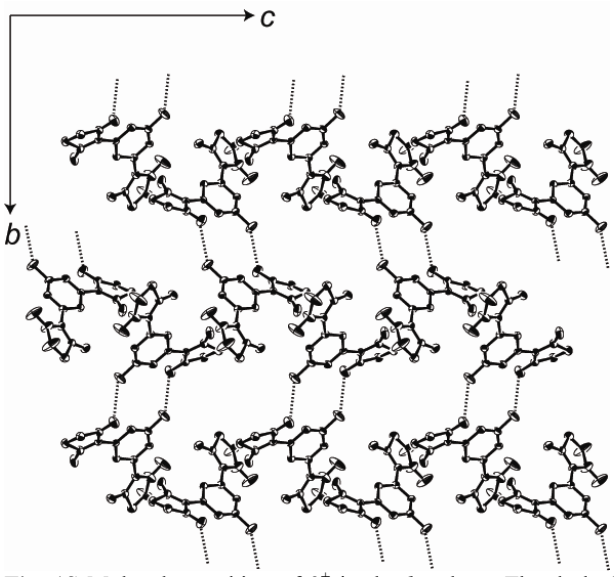
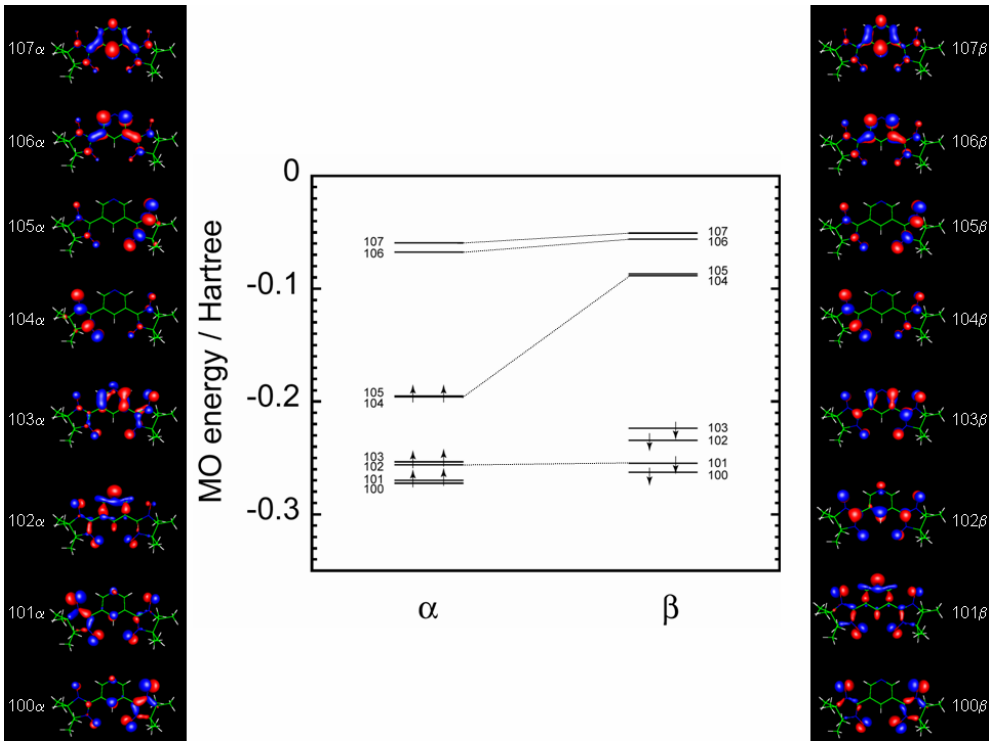
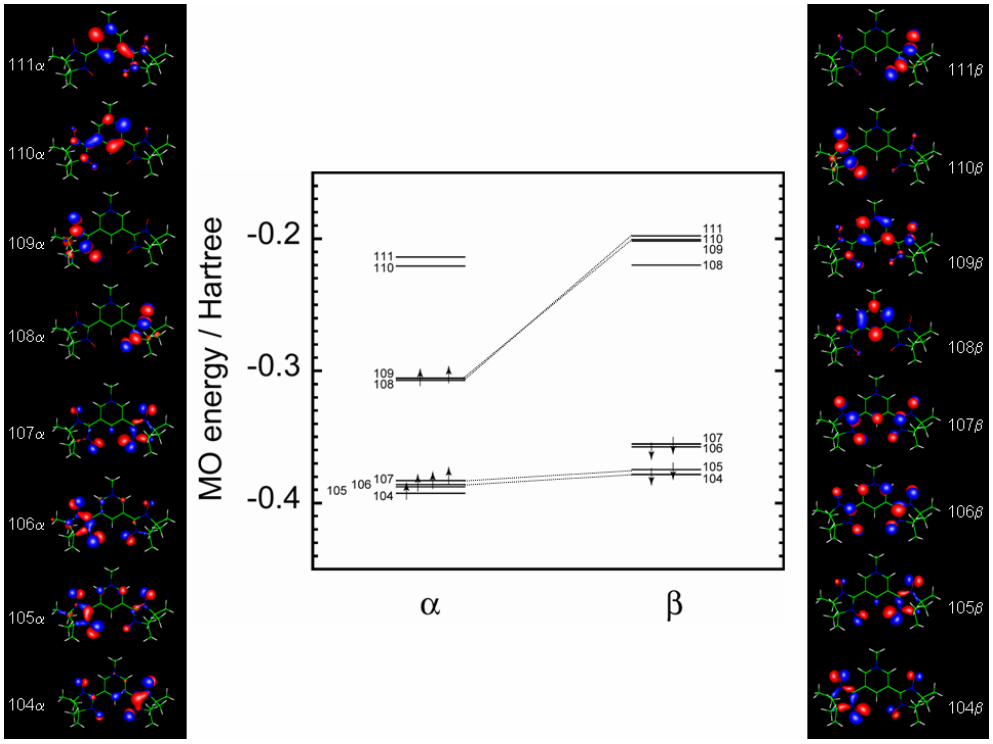


Fig. 1S Molecular packing of $\mathbf{2}^{+}$ in the *bc* plane. The dashed lines represent the intermolecular contact with the O2-C20 distance of 3.066(5) Å. The methyl groups of nitronylnitroxide and the hydrogen atoms are omitted for clarity.

(a)



(b)



15

Fig. 2S Energies and orbital pictures of the topmost occupied and low-lying unoccupied orbitals for the neutral biradical **1**A (a) and the cation $\mathbf{2}^{+}$ (b) calculated by the DFT method. The α orbitals are combined by the dashed lines with the β orbitals of the same symmetry. The electronic configuration of the triplet ground state is depicted by the arrows.

Table 1S Atomic spin densities ρ of the biradical **1** calculated at UB3LYP/6-31+G(d,p) level.[a]

1A				**1B**			
Atom	ρ	Atom	ρ	Atom	ρ	Atom	ρ
N1	0.032504	O3	0.332985	N6	0.033014	O7	0.329222
C1	-0.073596	O4	0.326429	C20	-0.071037	O8	0.333779
C2	0.049629	N4	0.299077	C21	0.068097	N9	0.294688
C3	-0.070092	N5	0.290230	C22	-0.071979	N10	0.287988
C4	0.053792	C13	-0.218368	C23	0.043406	C32	-0.212567
C5	-0.070963	C14	-0.003413	C24	-0.075673	C33	-0.004854
H1	0.003184	C15	-0.007185	H28	0.003405	C34	-0.007603
H2	0.002710	C16	0.014663	H29	0.002643	C35	-0.000727
H3	0.003626	C17	-0.005838	H30	0.003175	C36	0.008046
O1	0.321678	C18	-0.004610	O5	0.342267	C37	0.011259
O2	0.339274	C19	0.016641	O6	0.317346	C38	-0.002198
N2	0.292764	H16	0.001113	N7	0.307609	H43	-0.000340
N3	0.298932	H17	-0.000959	N8	0.278528	H44	-0.000438
C6	-0.220537	H18	-0.001091	C25	-0.218009	H45	0.000141
C7	0.003051	H19	-0.000369	C26	-0.012716	H46	-0.000496
C8	-0.018630	H20	-0.000200	C27	-0.001365	H47	0.000082
C9	-0.005008	H21	-0.000535	C28	0.012936	H48	-0.000449
C10	0.014431	H22	-0.000405	C29	-0.002573	H49	-0.000467
C11	0.017820	H23	-0.000606	C30	-0.002477	H50	-0.000046
C12	-0.005506	H24	-0.000184	C31	0.011913	H51	-0.000442
H4	-0.000593	H25	-0.001119	H31	-0.000330	H52	-0.000322
H5	-0.000164	H26	0.000634	H32	-0.000515	H53	-0.000427
H6	-0.000380	H27	-0.000858	H33	0.000541	H54	0.000053
H7	-0.001177			H34	-0.000476		
H8	-0.000914			H35	-0.000404		
H9	0.000675			H36	0.000254		
H10	-0.000932			H37	-0.000310		
H11	-0.001142			H38	0.000065		
H12	0.000654			H39	-0.000338		
H13	-0.000176			H40	-0.000033		
H14	-0.000368			H41	-0.000407		
H15	-0.000578			H42	-0.000440		

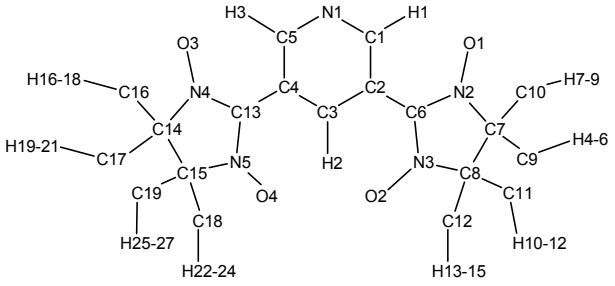
[a]The atom numbering scheme is given in Scheme 1S.

Table 2S Atomic spin densities ρ of the biradical $\mathbf{2}^{+}$ calculated at UB3LYP/6-31+G(d,p) level.[a]

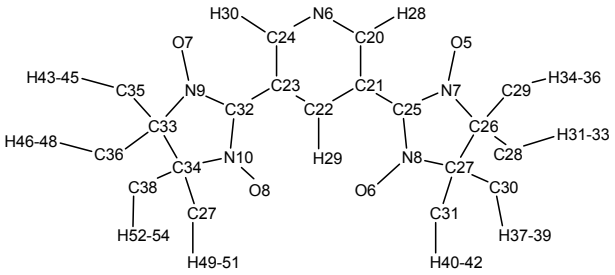
Atom	ρ	Atom	ρ
N1	0.031086	O3	0.331949
C1	-0.086977	O4	0.323624
C2	0.041397	N4	0.282446
C3	-0.086072	N5	0.296262
C4	0.055215	C13	-0.208426
C5	-0.052939	C14	-0.015999
H1	0.004097	C15	-0.000427
H2	0.002791	C16	0.020828
H3	0.002877	C17	-0.005133
O1	0.349388	C18	-0.020805
O2	0.322398	C19	0.044244
N2	0.282528	H16	-0.000441
N3	0.296188	H17	-0.000508
C6	-0.214563	H18	-0.000532
C7	-0.009670	H19	-0.000606
C8	0.005044	H20	-0.000628
C9	-0.004060	H21	0.000500
C10	0.011176	H22	0.001598
C11	0.007984	H23	-0.000866
C12	0.002016	H24	-0.000857
H4	-0.000378	H25	-0.001443
H5	-0.000514	H26	-0.000529
H6	0.000167	H27	-0.001313
H7	-0.000326	C20	-0.001091
H8	0.000018	H28	0.000163
H9	-0.000405	H29	0.000218
H10	0.000090	H30	0.000952
H11	-0.000448		
H12	-0.000585		
H13	-0.000271		
H14	-0.000022		
H15	-0.000411		

[a]The atom numbering scheme is given in Scheme 1S.

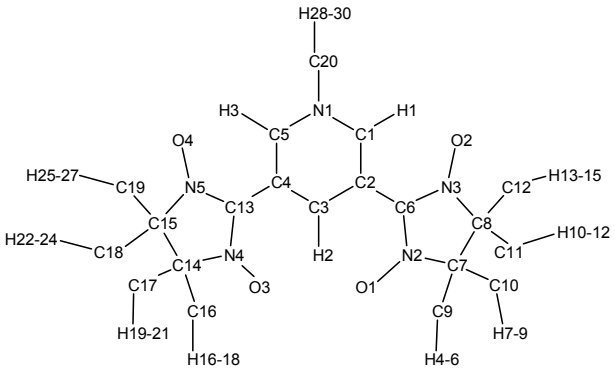
Scheme 1S Atom numbering schemes of the neutral biradical **1** and the cation biradical $\mathbf{2}^{+}$, corresponding to DFT-calculated spin density distribution in Table 1S and Table 2S.



1A



1B



2^{+}