Electronic Structure of Hole-Conducting States in Polyprolines

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Supporting Information to the paper

1. Complete references 9, 12, and 22

(9) Shih, C.; Museth, A. K.; Abrahamsson, M.; Blanco-Rodriguez, A. M.; Di Bilio, A. J.; Sudhamsu, J.; Crane, B. R.; Ronayne, K. L.; Towrie, M.; Vlcek, A.; Richards, J. H.; Winkler, J. R.; Gray, H. B. Tryptophan-accelerated Electron Flow Through Proteins. *Science* **2008,** *320*, 1760-1762.

(12) Glass, R. S.; Hug, G. L.; Schoneich, C.; Wilson, G. S.; Kuznetsova, L.; Lee, T. M.; Ammam, M.; Lorance, E.; Nauser, T.; Nichol, G. S.; Yamamoto, T. Neighboring Amide Participation in Thioether Oxidation: Relevance to Biological Oxidation. *J. Am. Chem. Soc.* **2009,** *131*, 13791-13805.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Gaussian, Inc.: Wallingford, CT, USA, 2009

2. Additional Figures S1 and S2

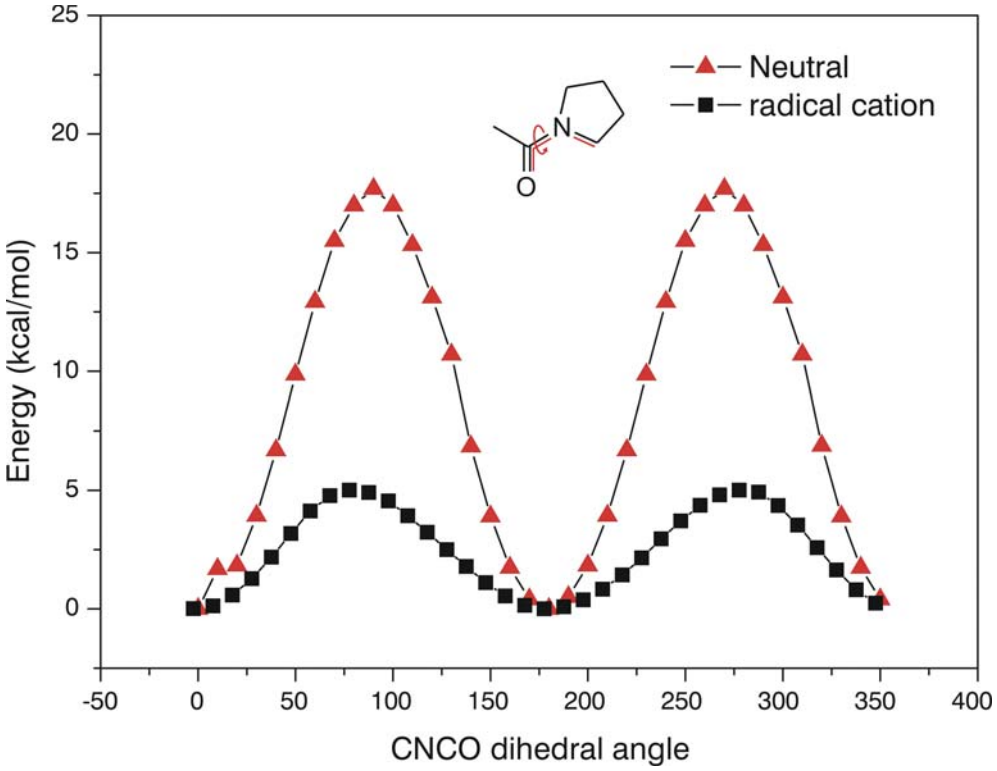

Figure S1: relaxed potential energy scan around the CNCO angle (depicted in red) in the neutral (black squares) and radical cation (red triangles) of N-acetylpyrrolydine.

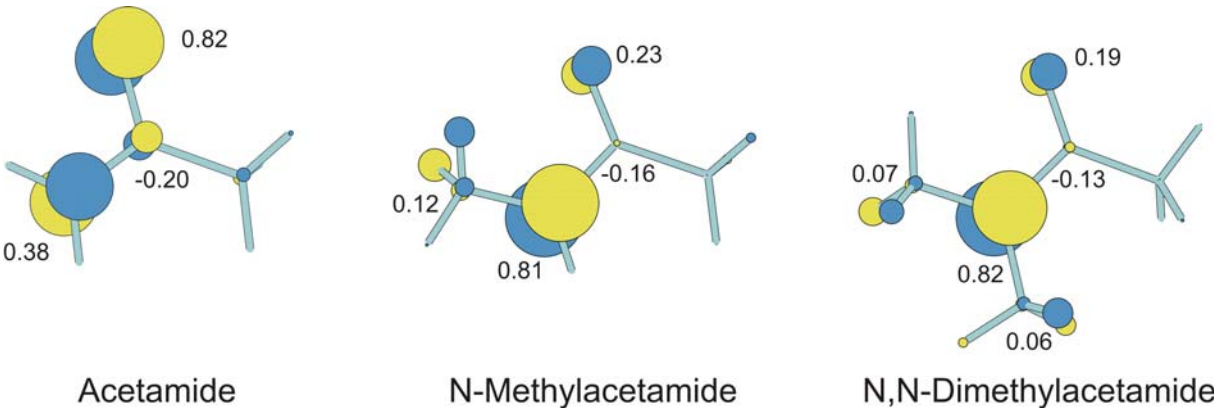

Figure S2: SOMO of Acetamide, N-Methylacetamide and N,N-Dimethylacetamide, together with the local spin densities on C, N and O atoms.

2. Additional Tables S1 and S2

Table S1: Relative energies and Ramachandran angles of the four chosen conformers of **2** calculated with M06-2X/6-31G*. The two different conformations of proline are shown in Figure 3.

	ϕ	ψ	cis/trans amide bond	Proline conformation	Relative energy (kcal/mol)
2A	-68	130	trans	1	0.0
2B	-46	-44	trans	2	4.4
2D	-57	130	trans	2	0.7
2G	-76	-13	trans	1	5.5
2H	-55	165	cis	2	3.4
2I	-50	-52	cis	2	2.8
2J	-66	170	cis	1	2.2
2K	-72	-10	cis	1	4.5

Table S2: Relative energies and Ramachandran angles of the four chosen conformers of the radical cation of **2** calculated with M06-2X/6-31G*. The two different conformations of proline are shown in Figure 3.

	ϕ	ψ	cis/trans amide bond	Proline conformation	Relative energy (kcal/mol)	Localization of SOMO
2A$^{\bullet+}$	-74	118	trans	1	0.0	hyperconjugative state
2B$^{\bullet+}$	-32	-21	trans	2	1.4	N∴O 2c-3e complex
2C$^{\bullet+}$	-40	178	trans	2	3.6	O∴O 2c-3e complex
2D$^{\bullet+}$	-74	120	trans	2	0.5	hyperconjugative state
2E$^{\bullet+}$	-27	-30	trans	1	3.2	N∴O 2c-3e complex
2F$^{\bullet+}$	-46	179	trans	1	4.1	O∴O 2c-3e complex
2G$^{\bullet+}$	-78	2	trans	1	6.2	hyperconjugative state
2H$^{\bullet+}$	-52	172	cis	2	5.5	N-centered
2I$^{\bullet+}$	-81	4	cis	1	7.6	hyperconjugative state
2J$^{\bullet+}$	-62	177	cis	1	9.1	hyperconjugative state

The geometries and total energies of all species mentioned in this paper are available from the authors on request.