Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

Supporting Information

69451 Weinheim, Germany

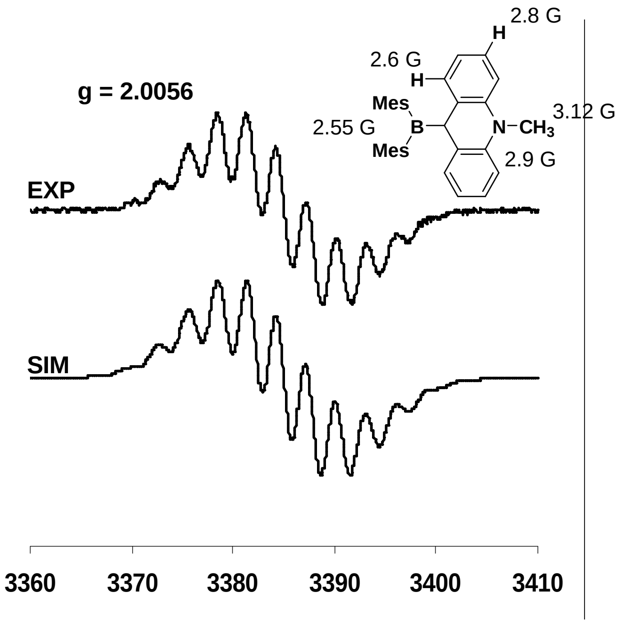
A 9-borylated acridinyl radical

*Ching-Wen Chiu and François P. Gabbaï**

General considerations: 9-Bromoacridine was synthesized by following the published procedure (C. Wolf, X. Mei, *J. Am. Chem. Soc.* **2003**, *125*, 10651-10658). Dimesitylboron fluoride and methyl triflate were purchased from Aldrich and used without further purification. Ether and hexane were dried by refluxing under N_2 atmosphere over Na/K and freshly distilled prior to use. CH_2Cl_2, acetonitrile were dried by passing through an alumina column under N_2 atmosphere. All the air sensitive compounds were handled under a N_2 atmosphere utilizing standard Schlenk and glovebox techniques. Elemental analyses were performed at Atlantic Microlab (Norcross, GA). The melting point was measured on samples in sealed capillaries and is uncorrected. NMR spectra were recorded on Varian Unity Inova FT NMR (499.95 MHz for ^1H, 160.4 MHz for ^{11}B, and 125.7 MHz for ^{13}C) spectrometer. Chemical shifts δ are given in ppm and are referenced against external Me_4Si (^1H, ^{13}C), and $BF_3•OEt_2$ (^{11}B).

Electrochemistry: Electrochemical experiments were performed with an electrochemical analyzer from CH Instruments (Model 610A) with a glassy carbon working electrode and a platinum auxiliary electrode at a scan rate of 300 mV/s. The reference electrode was built from a silver wire inserted in a small glass tube fitted with a porous vycor frit at the tip and filled with a CH_3CN solution containing (n-Bu)$_4$NPF$_6$ (0.1 M) and $AgNO_3$ (0.005 M). All three electrodes were immersed in a CH_2Cl_2 solution (8 mL) containing (n-Bu)$_4$NPF$_6$ (0.1 M) as a support electrolyte and [**1**][OTf] (0.001 M). The electrolyte was dried under vacuum prior to use. In all cases, ferrocene was used as an internal standard, and all reduction potentials are reported with respect to the $E_{1/2}$ of the Fc/Fc^+ redox couple.

EPR Measurement: EPR measurement was carried out in a Bruker EMX X-band spectrometer. **1**$^\bullet$ was generated by reduction of [**1**][OTf] in acetonitrile/hexane biphasic condition. The hexane phase was transferred to an EPR tube in glovebox. EPR spectrum was obtained at room temperature with a microwave power of 0.02 mW, modulation amplitude of 0.3G, time constant of 327.68 ms, and sweep time of 167.77 s. The hyperfine coupling constants were determined by computer simulation using WinEPR simfonia version 1.25 program. This simulation only account for the hyperfine coupling constant of the ^{11}B nucleus.



Experimental (top) and simulated (bottom) EPR spectrum of **1**$^{\bullet}$

Computational details: All calculations carried out on 1$^{\bullet}$ were performed using the Gaussian 03 suite of programs (Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.). DFT calculations were carried out by using the gradient-corrected Becke exchange functional (B3LYP) (A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648) and the Lee-Yang-Parr correlation functional (C. Lee, W. Yang, R.G. Parr, *Physical Review B* **1988**, *37*, 785 and B. Miehlich, A. Savin, H.; Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200) with a 6-31G basis set (W.J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys.* **1972**, 56, 2257). The geometry of **1**$^{\bullet}$ was fully optimized and the frequency calculation on the optimized geometry indicated the absence of imaginary frequencies.

Cartesian coordinates for the optimized geometry of $1^{\bullet}$:

C1	-0.46556	-0.84516	0.295175
C2	-0.23479	-2.07751	-0.4423
C3	0.310339	-2.07984	-1.75511
H4	0.586738	-1.13402	-2.1988
C5	0.506864	-3.24681	-2.48176
H6	0.932794	-3.19823	-3.47831
C7	0.133178	-4.48011	-1.92962
H8	0.257914	-5.39784	-2.49506
C9	-0.42667	-4.52803	-0.65461
H10	-0.75199	-5.48257	-0.262
C11	-0.60579	-3.35128	0.100402
N12	-1.14938	-3.40979	1.392493
C13	-1.62763	-2.25133	2.024971
C14	-2.43746	-2.35611	3.173781
H15	-2.76159	-3.32747	3.523641
C16	-2.86042	-1.21896	3.858558
H17	-3.48691	-1.32386	4.738325
C18	-2.47419	0.049275	3.403265
H19	-2.78269	0.941511	3.938019
C20	-1.69912	0.166289	2.257001
H21	-1.42105	1.151149	1.912613
C22	-1.27017	-0.96131	1.502116
C23	-0.68385	1.862672	-0.18907
C24	-1.95273	1.931851	-0.83957
C25	-2.64666	3.148568	-0.9087
H26	-3.60073	3.179157	-1.43004
C27	-2.15145	4.320466	-0.32319
C28	-0.91732	4.249394	0.334559
H29	-0.51561	5.144138	0.804911
C30	-0.17792	3.058839	0.402669
C31	-2.5964	0.71924	-1.48934
H32	-3.471	1.018674	-2.07633
H33	-2.93141	-0.00534	-0.73854
H34	-1.91438	0.185876	-2.16038
C35	-2.93764	5.611667	-0.37317
H36	-3.62127	5.696159	0.483252
H37	-3.54724	5.674389	-1.28121
H38	-2.27623	6.484555	-0.3473
C39	1.143868	3.094284	1.150088
H40	1.229561	2.277661	1.876072
H41	1.247055	4.035424	1.700308
H42	1.998636	3.006102	0.471342
C43	1.660946	0.553251	-0.69245
C44	2.029355	1.192395	-1.91624
C45	3.372813	1.240391	-2.31485
H46	3.623104	1.719174	-3.25901
C47	4.400178	0.698237	-1.53235
C48	4.044117	0.08891	-0.32458
H49	4.825119	-0.3271	0.307827
C50	2.709066	-0.00644	0.098059
C51	1.006093	1.817973	-2.84948
H52	0.15389	1.156174	-3.04116
H53	1.464863	2.050903	-3.81616

H54	0.596177	2.747266	-2.44028
C55	2.453941	-0.69931	1.42609
H56	2.034746	-1.70193	1.281314
H57	1.751652	-0.151	2.061879
H58	3.390485	-0.81043	1.983118
C59	5.840734	0.751151	-1.99014
H60	6.065997	-0.06267	-2.69348
H61	6.532168	0.653098	-1.14649
H62	6.064349	1.692772	-2.50449
C63	-1.22701	-4.69925	2.088283
H64	-1.12019	-4.53811	3.161927
H65	-0.40175	-5.33457	1.764508
H66	-2.1731	-5.22413	1.900985
B67	0.151081	0.510645	-0.18785

Optimized geometry of $1^{\bullet}$ and atom numbering scheme