SUPPORTING INFORMATION

The Azine Bridge as a Conjugation Stopper: An NMR Spectroscopic Study of Electron Delocalization in Acetophenone Azines.[‡]

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Table 1. Empirical and Experimental Aromatic ¹H Chemical Shifts for Symmetrical Acetophenone Azines **1 – 9** ^{a-c}

D = A	Empirical ³²		Experimental			
	H _o	H _m	H _o	H _m		
F	1	7.14	7.88	7.09	7.89	2.31
Cl	2	7.43	7.86	7.37	7.82	2.28
Br	3	7.58	7.80	7.53	7.75	2.27
I	4	7.79	7.67	7.74	7.62	2.26
NO ₂	5	8.35	8.14	8.27	8.06	2.35
CN	6	7.76	8.06	7.70	7.99	2.31
NH ₂ ^c	7	6.65	7.63	6.67	7.73	2.28
OCH ₃ ^d	8	6.92	7.79	6.94	7.88	2.32
OPh ^e	9	7.11	7.83	7.05	7.88	2.31

^a Chemical shifts in ppm relative to TMS. ^b H_o and H_m are the aromatic H atoms *ortho* and *meta* with respect to the donor and acceptor groups (Scheme 4). ^c Amino H atoms in **7**: broad signal at about 3.8 ppm. ^d Methoxy H atoms in **8** at 3.84 ppm. ^e Aromatic H atoms in the PhO group: 6.97 (H_o), 7.21 (H_m), and 7.03 ppm (H_p).

Table 2. ¹H NMR Chemical Shifts for the Unsymmetric Acetophenone Azines **10** – **27** ^{a-c}

D	A	H _o	H _m	CH ₃	'CH ₃	H _m '	H _o '	Other			
NH ₂	F	10	6.67	7.74	2.27	2.31	7.88	7.07	3.84		
	Cl	11	6.68	7.74	2.27	2.30	7.82	7.35	3.85		
	Br	12	6.68	7.73	2.26	2.30	7.76	7.51	3.85		
	I	13	6.67	7.71	2.28	2.26	7.61	7.75	3.85		
NO ₂		14	6.68	7.76	2.29	2.37	8.04	8.25	3.89		
	CN	15	6.68	7.75	2.27	2.33	7.98	7.67	3.88		
	F	16	6.92	7.86	2.32	2.30	7.89	7.08	3.84		
	Cl	17	6.92	7.86	2.30	2.29	7.82	7.36	3.84		
OCH ₃	Br	18	6.92	7.86	2.30	2.29	7.76	7.52	3.84		
	I	19	6.92	7.85	2.28	2.28	7.62	7.75	3.84		
	NO ₂	20	6.94	7.88	2.31	2.36	8.05	8.25	3.85		
	CN	21	6.92	7.87	2.32	2.29	7.99	7.69	3.85		
OPh	F	22	7.04	7.87	2.31	2.31	7.90	7.07	7.01	7.35	7.13
	Cl	23	7.05	7.87	2.30	2.30	7.83	7.35	7.01	7.35	7.13
	Br	24	7.04	7.87	2.29	2.29	7.76	7.52	7.01	7.34	7.13
	I	25	7.04	7.87	2.29	2.28	7.62	7.74	7.01	7.35	7.14
NO ₂		26	7.05	7.90	7.32	7.37	8.05	8.26	7.02	7.36	7.16
	CN	27	7.05	7.88	2.33	2.30	7.99	7.69	7.01	7.36	7.15

^a Chemical shifts in ppm relative to TMS. ^b H_o, H_o', H_m and H_m' refer to the H atoms depicted in Scheme 4. ^c Entries under "Other" refer to the amino H atoms in **10-15**, the methoxy H atoms in **16-21**, and the aromatic H atoms in the PhO substituent of **22-27** (H_o', H_m', and H_p' are given from left to right).

Table 3. Empirical and Experimental ^{13}C Chemical Shifts for Symmetrical Acetophenone Azines **1 – 9** *a,b*

D = A	Empirical ³²					Experimental						
	C _i	C _o	C _m	C _p		C _i	C _o	C _m	C _p	C _{az}	CH ₃	
F	1	167.7	115.4	130.2	133.0		163.8	115.2	128.5	134.5	157.4	14.9
Cl	2	139.2	128.8	130	135.5		135.8	128.5	127.9	136.7	157.3	14.9
Br	3	127.1	131.6	130.2	135.8		124.2	131.5	128.2	137.1	157.3	14.8
I	4	98.8	137.3	130.2	136.3		96.2	137.5	128.3	137.7	157.3	14.8
NO ₂	5	152.8	123.5	129.5	143.5		148.6	123.7	127.5	143.6	156.5	15.3
CN	6	117.2	132.0	129.3	141.7		113.5	132.5	127.5	142.4	156.8	15.1
NH ₂	7	151.1	115.0	129.4	127.4		148.6	114.5	128.3	129.3	158.4	14.5
OCH ₃	8	164.3	114.0	129.6	129.7		160.8	113.6	128.0	131.3	157.8	14.8
OPh ^c	9	160.5	117.2	128.3	130.5		158.8	119.4	129.8	133.4	157.7	14.9

^a Chemical shifts in ppm relative to TMS. ^b C_i , C_o , C_m and C_p refer to the carbon atoms depicted in Scheme 4. ^c PhO group: 156.1 (C_i), ether, 117.3 (C_o), 128.2 (C_m), and 121.6 (C_p).

Table 4. ¹³C NMR Chemical Shifts for the Unsymmetric Acetophenone Azines **10** – **27** ^{a-b}

D	A	C _i	C _o	C _m	C _p	C _{az}	H ₃ C	H ₃ C'	C _{az} '	C _p '	C _m '	C _o '	C _i '	
NH ₂	F	10	148.0	114.5	128.1	128.8	158.5	14.7	14.9	157.1	135.0	128.5	115.2	163.7
	Cl	11	148.1	114.4	128.2	128.7	158.6	14.7	14.7	157.0	137.2	127.9	128.5	135.4
	Br	12	148.1	114.4	128.2	128.7	158.5	14.7	14.7	157.1	137.7	128.1	131.4	123.8
	I	13	148.1	114.4	128.2	128.7	158.5	14.6	14.7	157.2	138.2	128.2	137.4	95.7
	NO ₂	14	148.2	114.4	128.3	128.3	159.2	14.8	14.9	156.2	144.6	127.3	123.5	148.4
OCH ₃ ^d	CN ^c	15	148.4	114.4	128.3	128.3	159.1	14.7	14.8	156.5	142.8	127.1	132.1	112.6
	F	16	161.0	113.7	128.1	131.1	158.1	14.8	14.9	157.2	134.8	128.5	115.3	163.7
	Cl	17	161.0	113.7	128.1	131.0	158.0	14.8	14.8	157.1	137.0	127.9	128.5	135.5
	Br	18	161.0	113.7	128.1	131.0	158.1	14.7	14.9	157.2	137.5	128.1	131.5	123.9
	I	19	161.0	113.7	128.1	131.0	158.0	14.7	14.9	157.3	138.1	128.3	137.5	95.9
OPh ^e	NO ₂	20	161.2	113.8	128.3	130.6	158.6	14.9	15.0	156.3	144.4	127.3	123.6	148.3
	CN ^c	21	161.2	113.7	128.2	130.7	158.5	14.7	14.9	156.5	142.6	127.0	132.1	112.7
	F	22	158.9	119.4	129.8	133.3	157.9	14.9	14.9	157.3	134.6	128.5	115.3	163.8
	Cl	23	158.9	119.4	129.8	133.2	157.8	14.8	15.0	157.2	136.9	127.9	128.5	135.6
	Br	24	158.9	119.4	129.8	133.1	157.8	14.8	14.9	157.2	137.3	128.1	131.4	124.0
	I	25	159.0	119.4	129.9	133.2	157.7	14.7	15.0	157.4	138.0	128.3	137.5	96.0
	NO ₂	26	159.3	119.5	129.9	132.7	158.3	15.0	15.1	156.3	144.2	127.4	123.6	148.3
	CN ^c	27	159.1	119.4	129.9	132.8	158.1	14.8	15.1	156.5	142.4	127.1	132.1	112.8

^a Chemical shifts in ppm relative to TMS. ^b C_i, C_i', C_o, C_o', C_m, C_m', C_p and C_p' refer to the carbon atoms depicted in Scheme 4.^c CN carbon in **15** at 118.8, in **21** at 118.7, and in **27** at 118.7 ppm. ^e PhO group (in ppm for C_i', C_o', C_m', and C_p') in **22**: 156.6, 118.1, 128.2, 123.8; in **23**: 156.5, 118.1, 128.3, 123.8; in **24**: 156.5, 118.1, 128.2, 123.7; in **25**: 156.6, 118.1, 128.3, 123.8; in **26**: 156.4, 118.1, 128.4, 123.9; in **27**: 156.4, 118.0, 128.3, 123.9.