Supporting Information

for

Nature of Chemical Bonding and Metalloaromaticity of $Na_2[(MArx')_3]$ (M=B, Al, Ga; Arx′=C_6H_3-2,6-$(C_6H_5)_2$)

Xiaoyan Li Jie Sun Yanli Zeng Zheng Sun Shijun Zheng

Lingpeng Meng*

Institute of Computational Quantum Chemistry, College of chemistry, Hebei Normal University, Yuhua Road, Shijiazhuang, 050016, China

Table of contents:

Figure S1. Geometry and atom numbering scheme of Arx'

Figure S2. ELF isosurfaces of $[(MH)_3]^{2-}$ (M=B, Al, Ga).

Figure S3. Orbital plots of $Na_2[(MArx')_3]$ (M=B, Al, Ga).

Table S1. Cartesian coordinate of the optimized geometry for $Na_2[(MArx')_3]$ (M=B, Al, Ga).

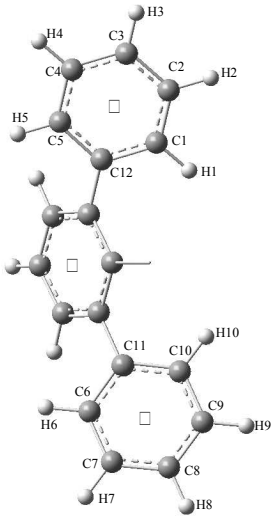


Figure S1. Geometry and atom numbering scheme of Arx'

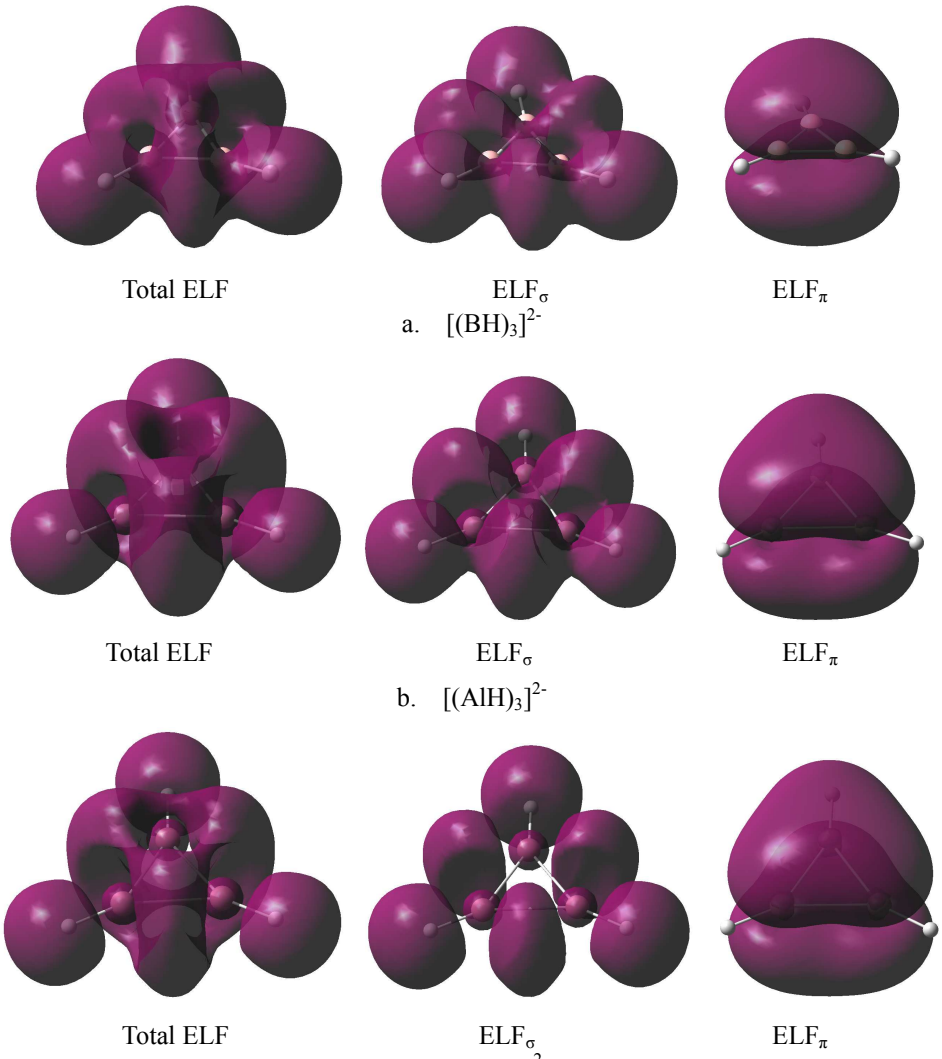
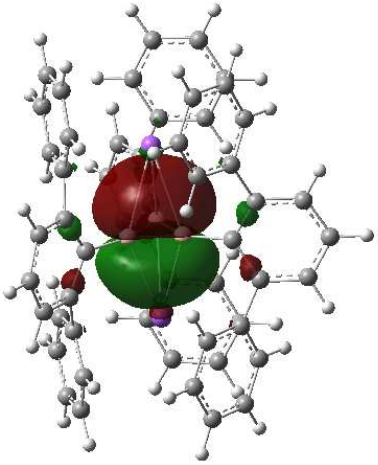
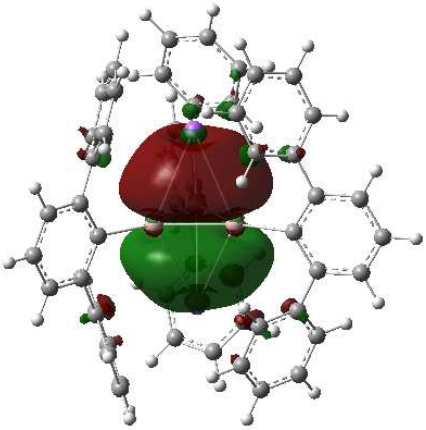


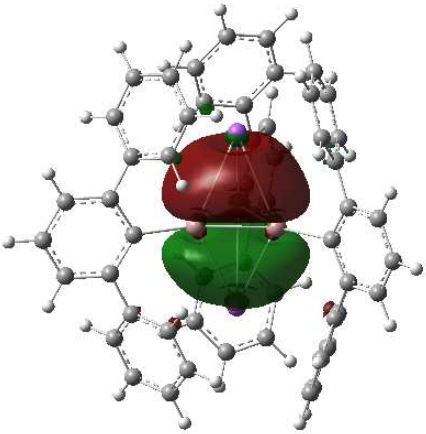
Figure S2. ELF isosurfaces of $[(MH)_3]^{2-}$ (M=B, Al, Ga).



a. $Na_2[(BArx')_3]$ (HOMO-2)



b. $Na_2[(AlArx')_3]$ (HOMO)



c. $Na_2[(GaArx')_3]$ (HOMO)

Figure S3. Orbital plots of $Na_2[(MArx')_3]$ (M=B, Al, Ga).

Table S1. Cartesian coordinate of the optimized geometry for $Na_2[(MArx')_3]$ (M=B,Al,Ga).

$Na_2[(BArx')_3]$

B	0.922765	-0.152090	0.000000
B	-0.323373	0.874426	0.000000
B	-0.588458	-0.716694	0.000000
Na	0.001628	-0.004394	2.660832
Na	0.001628	-0.004394	-2.660832
C	-1.358028	-2.082356	0.000000
C	-1.881640	-4.181407	1.190760
C	-1.881640	-4.181407	-1.190760
C	-1.933531	-4.895186	0.000000
H	-2.085625	-4.690288	2.126963
H	-2.085625	-4.690288	-2.126963
H	-2.114930	-5.963602	0.000000
C	2.490427	-0.136533	0.000000
C	4.572228	0.453364	-1.190578
C	4.572228	0.453364	1.190578
C	5.218279	0.761161	0.000000
H	5.114935	0.530083	-2.126856
H	5.114935	0.530083	2.126856
H	6.236176	1.133086	0.000000
C	-1.116288	2.227841	0.000000
C	-2.657772	3.746992	1.190580
C	-2.657772	3.746992	-1.190580
C	-3.242861	4.159098	0.000000
H	-2.993084	4.179897	2.127235
H	-2.993084	4.179897	-2.127235
H	-4.068317	4.861279	0.000000
C	2.787241	-0.575636	2.508618
C	2.986104	0.108116	3.720588
C	2.290826	-1.892590	2.579643
C	2.721501	-0.497494	4.949401
C	2.048349	-2.502978	3.806661
C	2.261334	-1.810410	5.000025
H	2.886415	0.056887	5.866796
H	1.709736	-3.532323	3.830302
C	2.787241	-0.575636	-2.508618
C	2.290826	-1.892590	-2.579643
C	2.986104	0.108116	-3.720588
C	2.048349	-2.502978	-3.806661

C	2.721501	-0.497494	-4.949401
C	2.261334	-1.810410	-5.000025
H	1.709736	-3.532323	-3.830302
H	2.886415	0.056887	-5.866796
C	3.259460	-0.032512	1.205299
C	3.259460	-0.032512	-1.205299
C	-0.888000	2.695805	2.510900
C	-1.585703	2.513238	3.717369
C	0.499867	2.926797	2.590633
C	-0.935641	2.577927	4.950205
C	1.142527	3.015042	3.821951
C	0.430086	2.841519	5.010136
H	-1.502576	2.433003	5.863317
H	2.202131	3.240471	3.853643
C	-0.888000	2.695805	-2.510900
C	0.499867	2.926797	-2.590633
C	-1.585703	2.513238	-3.717369
C	1.142527	3.015042	-3.821951
C	-0.935641	2.577927	-4.950205
C	0.430086	2.841519	-5.010136
H	2.202131	3.240471	-3.853643
H	-1.502576	2.433003	-5.863317
C	-1.588743	2.843063	1.205223
C	-1.588743	2.843063	-1.205223
C	-1.894394	-2.117434	2.505700
C	-1.399536	-2.620629	3.721342
C	-2.800690	-1.040089	2.569099
C	-1.802729	-2.088347	4.946514
C	-3.219293	-0.525381	3.792328
C	-2.723753	-1.045065	4.989516
H	-1.403529	-2.500132	5.866982
H	-3.951893	0.273340	3.810127
C	-1.894394	-2.117434	-2.505700
C	-2.800690	-1.040089	-2.569099
C	-1.399536	-2.620629	-3.721342
C	-3.219293	-0.525381	-3.792328
C	-1.802729	-2.088347	-4.946514
C	-2.723753	-1.045065	-4.989516
H	-3.951893	0.273340	-3.810127
H	-1.403529	-2.500132	-5.866982
C	-1.651408	-2.800491	1.205050

C	-1.651408	-2.800491	-1.205050
H	-3.056125	-0.645131	-5.940584
H	0.933103	2.915733	-5.967426
H	2.076152	-2.290706	-5.953951
H	2.134287	-2.442303	-1.659837
H	3.367992	1.120740	-3.695181
H	1.057894	3.074157	-1.674264
H	-2.652688	2.333951	-3.684369
H	-3.199864	-0.638799	-1.645883
H	-0.704312	-3.450191	-3.702152
H	2.076152	-2.290706	5.953951
H	-3.056125	-0.645131	5.940584
H	0.933103	2.915733	5.967426
H	1.057894	3.074157	1.674264
H	-3.199864	-0.638799	1.645883
H	-2.652688	2.333951	3.684369
H	-0.704312	-3.450191	3.702152
H	2.134287	-2.442303	1.659837
H	3.367992	1.120740	3.695181

$Na_2[(AlArx')_3]$

Al	1.151195	-0.892101	0.000000
Al	0.196985	1.443015	0.000000
Al	-1.348180	-0.550914	0.000000
Na	0.000000	0.000000	2.839892
Na	0.000000	0.000000	-2.839892
C	2.877458	-2.030681	0.000000
C	4.888313	-2.798402	1.197308
C	4.888313	-2.798402	-1.197308
C	5.550139	-3.035873	0.000000
H	5.381996	-3.020129	2.137938
H	5.381996	-3.020129	-2.137938
H	6.562063	-3.425655	0.000000
C	0.319893	3.507292	0.000000
C	-0.020669	5.632604	-1.197308
C	-0.020669	5.632604	1.197308
C	-0.145926	6.324497	0.000000
H	-0.075490	6.171010	-2.137938
H	-0.075490	6.171010	2.137938
H	-0.314327	7.395740	0.000000
C	-3.197350	-1.476611	0.000000

C	-4.867644	-2.834202	1.197308
C	-4.867644	-2.834202	-1.197308
C	-5.404212	-3.288625	0.000000
H	-5.306507	-3.150881	2.137938
H	-5.306507	-3.150881	-2.137938
H	-6.247735	-3.970085	0.000000
C	0.373403	3.603213	2.539177
C	-0.553182	3.828548	3.568972
C	1.486168	2.795079	2.820680
C	-0.380103	3.266728	4.832412
C	1.666540	2.237374	4.087317
C	0.730815	2.465649	5.097805
H	-1.109875	3.458834	5.611629
H	2.545108	1.634043	4.285849
C	0.373403	3.603213	-2.539177
C	1.486168	2.795079	-2.820680
C	-0.553182	3.828548	-3.568972
C	1.666540	2.237374	-4.087317
C	-0.380103	3.266728	-4.832412
C	0.730815	2.465649	-5.097805
H	2.545108	1.634043	-4.285849
H	-1.109875	3.458834	-5.611629
C	0.215321	4.250197	1.204404
C	0.215321	4.250197	-1.204404
C	-3.307176	-1.478230	2.539177
C	-3.039029	-2.393343	3.568972
C	-3.163693	-0.110480	2.820680
C	-2.639018	-1.962543	4.832412
C	-2.770893	0.324579	4.087317
C	-2.500722	-0.599920	5.097805
H	-2.440500	-2.690597	5.611629
H	-2.687676	1.387107	4.285849
C	-3.307176	-1.478230	-2.539177
C	-3.163693	-0.110480	-2.820680
C	-3.039029	-2.393343	-3.568972
C	-2.770893	0.324579	-4.087317
C	-2.639018	-1.962543	-4.832412
C	-2.500722	-0.599920	-5.097805
H	-2.687676	1.387107	-4.285849
H	-2.440500	-2.690597	-5.611629
C	-3.788439	-1.938625	1.204404

C	-3.788439	-1.938625	-1.204404
C	2.933773	-2.124983	2.539177
C	3.592210	-1.435205	3.568972
C	1.677525	-2.684598	2.820680
C	3.019121	-1.304185	4.832412
C	1.104352	-2.561953	4.087317
C	1.769907	-1.865729	5.097805
H	3.550375	-0.768237	5.611629
H	0.142568	-3.021149	4.285849
C	2.933773	-2.124983	-2.539177
C	1.677525	-2.684598	-2.820680
C	3.592210	-1.435205	-3.568972
C	1.104352	-2.561953	-4.087317
C	3.019121	-1.304185	-4.832412
C	1.769907	-1.865729	-5.097805
H	0.142568	-3.021149	-4.285849
H	3.550375	-0.768237	-5.611629
C	3.573118	-2.311572	1.204404
C	3.573118	-2.311572	-1.204404
H	1.328617	-1.779906	-6.084579
H	-2.205752	-0.260664	-6.084579
H	0.877135	2.040569	-6.084579
H	2.226217	2.627460	-2.047956
H	-1.423133	4.444042	-3.368969
H	-3.388556	0.614231	-2.047956
H	-3.137087	-3.454490	-3.368969
H	1.162339	-3.241691	-2.047956
H	4.560220	-0.989552	-3.368969
H	0.877135	2.040569	6.084579
H	1.328617	-1.779906	6.084579
H	-2.205752	-0.260664	6.084579
H	-3.388556	0.614231	2.047956
H	1.162339	-3.241691	2.047956
H	-3.137087	-3.454490	3.368969
H	4.560220	-0.989552	3.368969
H	2.226217	2.627460	2.047956
H	-1.423133	4.444042	3.368969

$Na_2[(GaArx')_3]$

Ga	0.974798	-1.055525	0.000000
Ga	0.426713	1.371963	0.000000
Ga	-1.401511	-0.316437	0.000000
Na	0.000000	0.000000	2.808067
Na	0.000000	0.000000	-2.808067
C	2.313542	-2.675262	0.000000
C	3.271306	-4.595622	1.197728
C	3.271306	-4.595622	-1.197728
C	3.573421	-5.230166	0.000000
H	3.539869	-5.065779	2.138354
H	3.539869	-5.065779	-2.138354
H	4.062055	-6.198215	0.000000
C	1.160073	3.341217	0.000000
C	2.344272	5.130845	-1.197728
C	2.344272	5.130845	1.197728
C	2.742746	5.709756	0.000000
H	2.617159	5.598506	-2.138354
H	2.617159	5.598506	2.138354
H	3.336784	6.616950	0.000000
C	-3.473616	-0.665956	0.000000
C	-5.615578	-0.535223	1.197728
C	-5.615578	-0.535223	-1.197728
C	-6.316167	-0.479590	0.000000
H	-6.157028	-0.532726	2.138354
H	-6.157028	-0.532726	-2.138354
H	-7.398839	-0.418735	0.000000
C	1.148194	3.440980	2.538390
C	-0.199922	3.174028	2.823165
C	2.087056	3.250572	3.563709
C	-0.593447	2.733177	4.087103
C	1.698184	2.804716	4.825620
C	0.355151	2.540381	5.093484
H	-1.643200	2.551395	4.287544
H	2.443714	2.668868	5.601768
C	1.148194	3.440980	-2.538390
C	2.087056	3.250572	-3.563709
C	-0.199922	3.174028	-2.823165
C	1.698184	2.804716	-4.825620
C	-0.593447	2.733177	-4.087103

C	0.355151	2.540381	-5.093484
H	2.443714	2.668868	-5.601768
H	-1.643200	2.551395	-4.287544
C	1.559389	3.968044	1.205268
C	1.559389	3.968044	-1.205268
C	-3.554073	-0.726124	2.538390
C	-2.648828	-1.760152	2.823165
C	-3.858606	0.182158	3.563709
C	-2.070277	-1.880528	4.087103
C	-3.278047	0.068312	4.825620
C	-2.377610	-0.962621	5.093484
H	-1.387972	-2.698751	4.287544
H	-3.533165	0.781884	5.601768
C	-3.554073	-0.726124	-2.538390
C	-3.858606	0.182158	-3.563709
C	-2.648828	-1.760152	-2.823165
C	-3.278047	0.068312	-4.825620
C	-2.070277	-1.880528	-4.087103
C	-2.377610	-0.962621	-5.093484
H	-3.533165	0.781884	-5.601768
H	-1.387972	-2.698751	-4.287544
C	-4.216121	-0.633552	1.205268
C	-4.216121	-0.633552	-1.205268
C	2.405878	-2.714855	2.538390
C	2.848750	-1.413877	2.823165
C	1.771550	-3.432730	3.563709
C	2.663724	-0.852649	4.087103
C	1.579863	-2.873028	4.825620
C	2.022459	-1.577760	5.093484
H	3.031173	0.147356	4.287544
H	1.089451	-3.450752	5.601768
C	2.405878	-2.714855	-2.538390
C	1.771550	-3.432730	-3.563709
C	2.848750	-1.413877	-2.823165
C	1.579863	-2.873028	-4.825620
C	2.663724	-0.852649	-4.087103
C	2.022459	-1.577760	-5.093484
H	1.089451	-3.450752	-5.601768
H	3.031173	0.147356	-4.287544
C	2.656732	-3.334492	1.205268
C	2.656732	-3.334492	-1.205268

H	1.887857	-1.144953	-6.078574
H	-1.935487	-1.062455	-6.078574
H	0.047630	2.207409	-6.078574
H	3.134321	3.445946	-3.361833
H	-0.943763	3.340093	-2.053867
H	-4.551437	0.991429	-3.361833
H	-2.420724	-2.487369	-2.053867
H	1.417116	-4.437375	-3.361833
H	3.364487	-0.852724	-2.053867
H	0.047630	2.207409	6.078574
H	1.887857	-1.144953	6.078574
H	-1.935487	-1.062455	6.078574
H	-4.551437	0.991429	3.361833
H	1.417116	-4.437375	3.361833
H	-2.420724	-2.487369	2.053867
H	3.364487	-0.852724	2.053867
H	3.134321	3.445946	3.361833
H	-0.943763	3.340093	2.053867

Full References:

[25] Frisch M. J.; Trucks G. W.; Schlegel H. B.; Scuseria G. E.; Robb M. A.; Cheeseman J. R.; Zakrzewski V. G.; Montgomery Jr. J. A.; Stratmann R. E.; Burant J. C.; Dapprich S.; Millam J. M.; Daniels A. D.; Kudin K. N.; Strain M. C.; Farkas O.; Tomasi J.; Barone V.; Cossi M.; Cammi R.; Mennucci B.; Pomelli C.; Adamo C.; Clifford S.; Ochterski J.; Petersson G. A.; Ayala P. Y.; Cui Q.; Morokuma K.; Malick D. K.; Rabuck A. D.; Raghavachari K.; Foresman J. B.; Cioslowski J.; Ortiz J. V.; Stefanov B. B.; Liu G.; Liashenko A.; Piskorz P.; Komaromi I.; Gomperts R.; Martin R. L.; Fox D. J.; Keith T.; Al-Laham M. A.; Peng C. Y.; Nanayakkara A.; Gonzalez C.; Challacombe M.; Gill P. M. W.; Johnson B.; Chen W.; Wong M. W.; Andres J. L.; Gonzalez C.; Head-Gordon M.; Replogle E. S.; Pople J. A. Gaussian 03, Revision D.01, Gaussian, Inc., Wallingford CT., **2004**.