Electronic Supplementary Information

Theoretical Calculations

Hybrid DFT calculations on the benzo-fused heterocyclic anions were performed using the GAMESS-UK software utilising the B3LYP functional and all-electron DZVP basis set.

NBO analysis was carried out using the nbo routine within the GAMESS-UK software utilising the **reson** keyword to accommodate the significant delocalisation in the structures. The NBO analysis attempts to describe the bonding through a series of localised 2c,2e$^-$ bonds and lone pairs. Deviations from the Lewis structure arise from occupancies of antibonding and Rydberg states. For closed shell systems a satisfactory Lewis structure typically comprises a series of bonding valence orbitals and lone pairs with occupancies near the idealised 2.0. Rydberg and antibonding orbitals are typically empty (occupancy = 0.0). The relative occupancies of the Lewis and non-Lewis states thus provide an estimate of how well the structure can be described in terms of a Lewis model. The total percentage Lewis character for each derivative is presented in Table 1.

Table 1. Percentage Lewis character for the NBO analysis of the group 15 heterocycles.

$C_6H_4N_3^-$	$C_6H_4N_2P^-$	$C_6H_4N_2As^-$	$C_6H_4N_2Sb^-$
96.2%	96.6%	96.8%	97.3%

For the more polar As structure no significant Lewis 2c,2e$^-$ As-N bonding was detected, although second order perturbation analysis reveals significant non-Lewis bonding interactions between the $C_6H_4N_2$ and As fragments. These will be discussed more fully in a future paper. Attempts to force a Lewis structure containing an N-As single bond using the **$choose** keyword led to structures with significantly lower Lewis character (Table 2). In the case of Sb, weak strongly polar π-bonding was detected within the sensitivity of the NBO method but the polarity of the Sb-N σ bond was found to be sufficiently high that it was not registered using the NBO method which assumes a 2c,2e$^-$ bond must have a minimum of 5% contribution from any one centre. The bond polarities, contributions of s and p orbitals on each centre towards bonding, orbital occupancies and bond orders for the heterocyclic ring in each compound are presented in Table 3-6 inclusive.

Table 2. Comparison of the percentage Lewis character for the NBO analysis of $C_6H_4N_2As^-$ with varying enforced electron distributions.

Forced As-N bond	Forced lone pairs on As	%Lewis character
N	N	94.9
Y	1	80.9
Y	2	81.7

Table 3. Details of NBO contributions for $C_6H_4N_3^-$

$C_6H_4N_3^-$						Bond polarity		Energy
C-C	Occupancy	%s(C)	%p(C)	%s(C)	%p(C)	(C)	(C)	
σ	1.9962	31.7	68.3	31.7	68.3	0.5	0.5	-0.475
σ*	0.0662	31.8	68.3	31.7	68.3	0.5	-0.5*	0.678
π	-	-	-	-	-	-	-	
π*	-	-	-	-	-	-	-	
Net σ	0.9651							
Net π	-							
Total BO	0.9650							
C-N	Occupancy	%s(C)	%p(C)	%s(N)	%p(N)	(C)	(N)	
σ	1.9826	30.9	69.1	33.0	67.0	0.425	0.575	-0.599
σ*	0.0388	30.9	69.1	33.0	67.0	0.575	-0.425*	0.667
π	1.7297	0	100	0	100	0.389	0.611	-0.107
π*	0.5667	0	100	0	100	0.611	-0.389*	0.195
Net σ	0.97190							
Net π	0.5815							
Total BO	1.5534							
N-N'	Occupancy	%s(N)	%p(N)	%s(N')	%p(N')	(N)	(N')	
σ	1.9796	26.4	73.6	27.4	72.6	0.505	0.495	-0.641
σ*	0.0378	26.4	73.6	27.4	72.6	0.495	-0.505*	0.605
π	1.8528	0	100	0	100	0.553	0.447	-0.136
π*	0.5651	0	100	0	100	0.447	-0.553*	0.147
Net σ	0.9709							
Net π	0.6439							
Total BO	1.6148							

Table 4 Details of NBO contributions for $C_6H_4N_2P^-$

$C_6H_4N_2P^-$						Bond polarity		Energy
C-C	Occupancy	%s(C)	%p(C)	%s(C)	%p(C)	(C)	(C)	
σ	1.9712	32.7	67.2	32.7	67.2	0.5	0.5	-0.474
σ*	0.0784	32.7	67.2	32.7	67.2	0.5	-0.5*	0.638
π	-	-	-	-	-	-	-	
π*	-	-	-	-	-	-	-	
Net σ	0.9464							
Net π	0							
Total BO	0.9464							
C-N	Occupancy	%s(C)	%p(C)	%s(N)	%p(N)	(C)	(N)	
σ	1.9853	31.0	68.9	37.0	62.8	0.409	0.591	-0.630
σ*	0.0269	31.0	68.9	37.0	62.8	0.591	-0.409*	0.657
π	1.7940	0	99.9	0	99.7	0.343	0.657	-0.123
π*	0.5751	0	99.9	0	99.7	0.657	-0.343*	0.184
Net σ	0.9792							
Net π	0.6095							
Total BO	1.5887							
N-P	Occupancy	%s(N)	%p(N)	%s(P)	%p(P)	(N)	(P)	
σ	1.9654	25.5	74.2	16.9	81.4	0.718	0.283	-0.641
σ*	0.0378	25.5	74.2	16.9	81.4	0.283	-0.718*	0.605
π	-	-	-	-	-	-	-	-
π*	-	-	-	-	-	-	-	-
Net σ	0.96380							
Net π	0							
Total BO	0.96380							

Table 5 Details of NBO contributions for $C_6H_4N_2As^-$

$C_6H_4N_2As^-$						Bond polarity		Energy
C-C	Occupancy	%s(C)	%p(C)	%s(C)	%p(C)	(C)	(C)	
σ	1.9357	32.5	67.4	32.5	67.4	0.5	0.5	-0.454
σ*	0.1282	32.5	67.4	32.5	67.4	0.5	-0.5	0.803
π	-	-	-	-	-	-	-	
π*	-	-	-	-	-	-	-	
Net σ	0.9037							
Net π	0							
Total BO	0.9037							
C-N	Occupancy	%s(C)	%p(C)	%s(N)	%p(N)	(C)	(N)	
σ	1.9608	33.4	66.5	65	34.4	0.398	0.602	-0.630
σ*	0.1287	33.4	66.5	65	34.4	0.602	-0.398*	0.657
π	1.8992	0	99.6	0	99.6	0.262	0.738	-0.123
π*	0.6166	0	99.6	0	99.6	0.738	-0.262*	0.184
Net σ	0.9161							
Net π	0.6413							
Total BO	1.5574							
N-As	Occupancy	%s(N)	%p(N)	%s(As)	%p(As)	(N)	(As)	
σ	-	-	-	-	-	-	-	-
σ*	-	-	-	-	-	-	-	-
π	-	-	-	-	-	-	-	-
π*	-	-	-	-	-	-	-	-
Net σ	-							
Net π	-							
Total BO	-							

Table 6 Details of NBO contributions for $C_6H_4N_2Sb^-$

$C_6H_4N_2Sb^-$						Bond polarity		Energy
C-C	Occupancy	%s(C)	%p(C)	%s(C)	%p(C)	(C)	(C)	
σ	1.9550	32.2	67.8	32.2	67.8	0.5	0.5	-0.464
σ*	0.0761	32.2	67.8	32.2	67.8	0.5	-0.5*	0.635
π	-	-	-	-	-	-	-	
π*	-	-	-	-	-	-	-	
Net σ	0.9464							
Net π	0							
Total BO	0.9464							
C-N	Occupancy	%s(C)	%p(C)	%s(N)	%p(N)	(C)	(N)	
σ	1.9589	30.5	69.4	43.9	55.9	0.612	0.388	-0.672
σ*	0.0885	30.5	69.4	43.9	55.9	0.388	-0.612*	0.648
π	1.8681	0	99.8	0	99.8	0.262	0.738	-0.142
π*	0.6484	0	99.8	0	99.8	0.738	-0.262*	0.179
Net σ	0.9352							
Net π	0.6099							
Total BO	1.5451							
N-Sb	Occupancy	%s(N)	%p(N)	%s(Sb)	%p(Sb)	(N)	(Sb)	
σ	-	-	-	-	-	-	-	-
σ*	-	-	-	-	-	-	-	-
π	1.8074	0	99.8	0	98.4	0.825	0.175	-0.099
π*	0.3388	0	99.8	0	98.4	0.175	-0.825*	0.173
Net σ	0.9638							
Net π	0							
Total BO	0.9638							