Electronic Supplementary Information

Linear BeNCO and OBeNC: kinetically stable neutral Be-bearing free molecules

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Captions of Supporting Figures and Tables

Table S1 Internal coordinates of the isomers and transition states, located at the B2PLYPD3/6-311+G(2df) level of theory, of the [Be,N,C,O] system.

Table S2 Internal coordinates of the isomers and transition states, located at the B3LYP-D3BJ/6-311+G(2df) level of theory, of the [Be,N,C,O] system.

Table S3 Internal coordinates of the isomers and transition states, located at the M06-2X-D3/*aug-cc-p*VQZ level of theory, of the [Be,N,C,O] system.

Table S4 Relative electronic energies (ΔE, in kcal mol^{-1}) with ZPVE correction, relative enthalpies (ΔH, in kcal mol^{-1}), and relative Gibbs free energies (ΔG, in kcal mol^{-1}) of the isomers, transition states, and dissociation fragments of the [Be,N,C,O] molecular system computed at different levels and the HOMO-LUMO gaps (HLGs, in eV) computed at the B2PLYPD3/6-311+G(2df).

Table S5 Relative electronic energies (E, in kcal mol^{-1}) with ZPVE correction of the four low-lying isomers computed at various DFT and CCSD(T) levels for the [Be,N,C,O] molecular system. The ground electronic states and Be-O-C angles (θ, degree, in parentheses) are given for only BeOCN; other three isomers are linear with $^2\Sigma$ ground electronic states.

Table S6 Valent molecular orbitals (VMOs) and the number of occupied electron (in parentheses), the contribution ((Cont., %)) of an atomic orbital (AO) to a MO, total contribution (TC) and composition proportion (CP) of all AOs of one atom to a MO, and orbital delocalization indices (ODI) computed at the CCSD(T)/*aug-cc-p*VQZ level of theory for BeNCO.

Table S7 Valent molecular orbitals (VMOs) and the number of occupied electron (in parentheses), the contribution ((Cont., %)) of an atomic orbital (AO) to a MO, total contribution (TC) and composition proportion (CP) of all AOs of one atom to a MO, and orbital delocalization indices (ODI) computed at the CCSD(T)/*aug-cc-p*VQZ level of theory for OBeNC.

Table S8 Local topological properties (in a.u.) of the electronic charge density distribution at bond critical points (BCPs) and bond delocalization indices (BDI), computed at the CCSD(T)/*aug-cc-p*VQZ level of theory, of BeNCO and OBeNC.

Table S9 CCSD/*aug-cc-p*CVTZ-computed vibrational spectra of BeNCO and OBeNC using ^{13}C, ^{15}N, and ^{18}O isotopes.

Fig. S1 Schematic structures and relative electronic energies (REs) with ZPVE correction of the isomers optimized at the B2PLYPD3/6-311+G(2df) (REs in parentheses), B3LYP-D3BJ/6-311+G(2df) (REs in square brackets), and M06-2X-D3/*aug-cc-p*VQZ (REs in curly brackets) levels of theory for the [Be,N,C,O] isomers in electronic quartet.

Fig. S2 Isomerization reaction potential energy profiles of the [Be,N,C,O] system constructed at the B3LYP-D3BJ/6-311+G(2df) (a) and M06-2X-D3/*aug-cc-p*VQZ (b) levels of theory.

Fig. S3 Schematic structures of some model compounds. The bond lengths (Å) optimized at the B3LYP-D3BJ/6-311++G(2df,2p) and B3LYP-D3BJ/6-311++G(d,p) are shown in blue and magenta, respectively.

Fig. S4 Valent molecular orbitals (isovalue = 0.06), computed at the CCSD(T)/*aug-cc-p*VQZ level of theory, of BeNCO.

Fig. S5 Valent molecular orbitals (isovalue = 0.06), computed at the CCSD(T)/*aug-cc-p*VQZ level of theory, of OBeNC.

Fig. S6 Electrostatic potential plots and Mulliken charges (|e|, in red), computed at the CCSD(T)/*cc-p*VQZ level of theory, of four model molecules. The bond distances in blue and wine were optimized at the CCSD(T)/*aug-cc-p*VQZ and B3LYP-D3BJ/6-311+G(2df) levels of theory, respectively.

Fig. S7 Valent molecular orbitals (isovalue = 0.06), computed at the CCSD(T)/*cc-p*VQZ level of theory, of four model molecules.

Table S1 Internal coordinates of the isomers and transition states, located at the B2PLYPD3/6-311+G(2df) level of theory, of the [Be,N,C,O] system.

BeNCO (**1**)	OBeNC (**2**)	Be-*c*OCN (**3**)	OBeCN (**4**)
Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,180.,0 Variables: r1=1.48851163 r2=1.19862813 r3=1.16655878	O Be,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,0.,0 C,4,r3,5,90.,2,180.,0 Variables: r1=1.46199517 r2=1.52075882 r3=1.17471673	Be O,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,a2,0 Variables: r1=1.41608722 r2=1.26544947 r3=1.16246514 a1=170.46427889 a2=179.52399415	O Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,0.,0 N,4,r3,5,90.,2,180.,0 Variables: r1=1.45659113 r2=1.649667 r3=1.15409231
BeCNO (**5**)	Be-*c*CNO (**6**)	NBeCO (**7**)	N-*c*BeOC (**8**)
Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,180.,0 Variables: r1=1.62538767 r2=1.17156357 r3=1.19339547	Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,0.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=3.61289024 r2=1.16896816 r3=1.30461788 a1=14.98121091 a2=183.96332942	N Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,180.,0 Variables: r1=1.50737259 r2=1.66575127 r3=1.1403759	N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,a2,0 Variables: r1=1.54849323 r2=1.60950949 r3=1.21372512 a1=155.31755879 a2=78.35646227
NBeOC (**9**)	Be-*c*NCO (**10**)	BeC-*c*NO (**11**)	BeNCO (**1q**)
N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,180.,0 Variables: r1=1.49626695 r2=1.52981214 r3=1.17498082	Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.51901126 r2=1.33196084 r3=1.3334134 a1=184.30350373 a2=71.97986724	Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.71194687 r2=1.24974194 r3=1.68982623 a1=143.53628643 a2=52.43847674	Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.54672301 r2=1.38353591 r3=1.18943348 a1=140.79191473 a2=128.84097867
BeOCN (**2q**)	BeONC (**3q**)	BeCNO (**4q**)	Be-*c*NCO (**5q**)
Be O,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,a2,0 Variables: r1=1.42814044 r2=1.29615946 r3=1.2876801 a1=165.27848668 a2=122.60345979	Be O,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,a2,0 Variables: r1=1.67570588 r2=1.42616777 r3=1.48487432 a1=62.07872619 a2=66.27207715	Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.62875726 r2=1.25164627 r3=1.24873751 a1=178.26119703 a2=126.66987496	Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.51621064 r2=1.30746476 r3=1.21400532 a1=186.62147096 a2=122.24204712

Be-*c*CNO (**6q**)	OBeNC (**7q**)	OBeCN (**8q**)	N-*c*BeOC (**9q**)
Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.64509219 r2=1.40959012 r3=1.41625329 a1=156.96099955 a2=57.9125082	O Be,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,180.,0 Variables: r1=1.48541583 r2=1.49998799 r3=1.2174237	O Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,180.,0 Variables: r1=1.47206153 r2=1.62443162 r3=1.2966569	N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,a2,0 Variables: r1=1.61490455 r2=1.61981219 r3=1.23786172 a1=145.7185159 a2=74.76943122
NBeOC (**10q**) N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,180.,0 Variables: r1=1.60671952 r2=1.43519626 r3=1.26385521	NBeCO (**11q**) N Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,180.,0 Variables: r1=1.61608655 r2=1.63569823 r3=1.16995835	**TS1** O Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,a2,0 Variables: r1=1.39372836 r2=1.6537636 r3=1.18241369 a1=68.8266695 a2=179.58449138	**TS2** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,0.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.78791721 r2=1.2058315 r3=1.24689023 a1=66.33686531 a2=145.99319027
TS3 Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,d1,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.63581592 r2=1.31062067 r3=1.7119902 a1=86.21034234 a2=49.30588318 d1=180.00481992	**TS4** N Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.45540639 r2=1.65356686 r3=1.13721538 a1=92.08884854 a2=188.33096452	**TS5** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,d1,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.59544052 r2=1.376805 r3=1.29738687 a1=83.57644118 a2=73.66485188 d1=133.27483467	**TS6** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,0.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.46148729 r2=2.64916765 r3=1.15977604 a1=59.35275232 a2=82.73780742
TS7 O Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,a2,0 Variables: r1=1.46388007 r2=1.66837335 r3=1.17143297 a1=175.72042972 a2=89.83691677	**TS8** Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,d1,0 O,4,r3,5,90.,2,a2,0 Variables: r1=2.20294661 r2=1.19813955 r3=1.40705221 a1=56.3455755 a2=143.45389791 d1=0.00016794	**TS9** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,0.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.63217729 r2=1.20089508 r3=1.86144323 a1=75.69352856 a2=109.26974277	**TS10** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,d1,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.7094689 r2=1.2020547 r3=2.53847945 a1=189.88086903 a2=24.05659838 d1=-1.49522766

TS11	**TS12**		
N Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.56812839 r2=1.7698943 r3=1.18628947 a1=181.65893585 a2=105.52999117	N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,a2,0 Variables: r1=1.4908116 r2=1.59295317 r3=1.21391961 a1=226.0873353 a2=83.49349777		

Table S2 Internal coordinates of the isomers and transition states, located at the B3LYP-D3BJ/6-311+G(2df) level of theory, of the [Be,N,C,O] system.

BeNCO (**1**)	OBeNC (**2**)	BeOCN (**3**)	OBeCN (**4**)
Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,180.,0 Variables: r1=1.49281869 r2=1.20175752 r3=1.16795853	O Be,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,0.,0 C,4,r3,5,90.,2,180.,0 Variables: r1=1.46482349 r2=1.52402716 r3=1.17975959	Be O,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,180.,0 Variables: r1=1.42164292 r2=1.26502448 r3=1.15864389	O Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,0.,0 N,4,r3,5,90.,2,180.,0 Variables: r1=1.46071921 r2=1.65104772 r3=1.15777275
BeCNO (**5**)	Be-*c*CNO (**6**)	NBeCO (**7**)	N-*c*BeOC (**8**)
Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,180.,0 Variables: r1=1.62924673 r2=1.17529873 r3=1.19565796	Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,0.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=3.65293007 r2=1.17419664 r3=1.30434411 a1=13.85252139 a2=184.56788465	N Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,180.,0 Variables: r1=1.50817541 r2=1.66646486 r3=1.14263689	N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,a2,0 Variables: r1=1.5451696 r2=1.62066576 r3=1.21547178 a1=157.8609506 a2=78.15082603
NBeOC (**9**)	Be-*c*NCO (**10**)	BeC-*c*NO (**11**)	BeNCO (**1q**)
N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,180.,0 Variables: r1=1.49627492 r2=1.53968284 r3=1.17920463	Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.52417851 r2=1.3379852 r3=1.33314178 a1=185.57511488 a2=72.20055945	Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.71765006 r2=1.25375085 r3=1.69800889 a1=143.57341785 a2=52.20250136	Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.53469234 r2=1.36016305 r3=1.19833211 a1=146.12051469 a2=129.23473746
BeOCN (**2q**)	BeONC (**3q**)	BeCNO (**4q**)	Be-*c*NCO (**5q**)
Be O,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,a2,0 Variables: r1=1.42350862 r2=1.29658625 r3=1.2846982 a1=168.84691375 a2=122.54896526	Be O,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,a2,0 Variables: r1=1.66334861 r2=1.43214509 r3=1.48264573 a1=62.19742121 a2=67.49607054	Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.6222952 r2=1.25621584 r3=1.25224261 a1=178.3845716 a2=126.73393708	Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.51049432 r2=1.29742089 r3=1.22188612 a1=185.38787305 a2=122.15041858

Be-*c*CNO (**6q**) Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.64111081 r2=1.41047196 r3=1.42105255 a1=156.86985551 a2=57.88081571	OBeNC (**7q**) O Be,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,180.,0 Variables: r1=1.4812914 r2=1.49665299 r3=1.22205395	OBeCN (**8q**) O Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,180.,0 Variables: r1=1.47206153 r2=1.62443162 r3=1.2966569	N-*c*BeOC (**9q**) N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,a2,0 Variables: r1=1.60857784 r2=1.61581027 r3=1.23558145 a1=145.65883259 a2=74.75371702
NBeOC (**10q**) N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,180.,0 Variables: r1=1.60211663 r2=1.43161125 r3=1.26202903	NBeCO (**11q**) N Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,180.,0 Variables: r1=1.61057553 r2=1.62943463 r3=1.16915273	**TS1** O Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,a2,0 Variables: r1=1.39165779 r2=1.65307789 r3=1.17965136 a1=70.39603441 a2=179.68394866	**TS2** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,0.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.80275493 r2=1.20729495 r3=1.24276537 a1=65.84696349 a2=147.929687
TS3 Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,d1,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.62827381 r2=1.30766156 r3=1.77047972 a1=88.85412272 a2=47.28843402 d1=180.00576406	**TS4** N Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.44459964 r2=1.69091737 r3=1.12829832 a1=107.58225608 a2=190.8456994	**TS5** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,d1,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.6017004 r2=1.37706889 r3=1.30502208 a1=83.7789527 a2=73.19804216 d1=132.81865185	**TS6** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,0.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.46286165 r2=2.58787846 r3=1.15970111 a1=61.00348308 a2=83.82231162
TS7 O Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,a2,0 Variables: r1=1.46132324 r2=1.66833844 r3=1.17487739 a1=176.2315139 a2=90.07522911	**TS8** Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,d1,0 O,4,r3,5,90.,2,a2,0 Variables: r1=2.08483581 r2=1.20547926 r3=1.41073547 a1=58.79539349 a2=139.92312433 d1=-0.00000235	**TS9** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,0.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.6350046 r2=1.19888253 r3=1.9209165 a1=75.89992522 a2=108.09370052	**TS10** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,d1,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.68316239 r2=1.20177201 r3=2.55532712 a1=188.29327092 a2=24.97337627 d1=0.12188418

TS11	**TS12**		
N Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.58628456 r2=1.73682843 r3=1.20343365 a1=186.12461783 a2=96.48954365	N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,a2,0 Variables: r1=1.49737396 r2=1.59571408 r3=1.209235 a1=220.68763724 a2=83.70768127		

Table S3 Internal coordinates of the isomers and transition states, located at the M06-2X-D3/*aug-cc-p*VQZ level of theory, of the [Be,N,C,O] system.

BeNCO (**1**)	OBeNC (**2**)	BeOCN (**3**)	OBeCN (**4**)
Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,180.,0 Variables: r1=1.48851163 r2=1.19862813 r3=1.16655878	O Be,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,0.,0 C,4,r3,5,90.,2,180.,0 Variables: r1=1.45969068 r2=1.52364452 r3=1.17191023	Be O,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,0.,0 N,4,r3,5,90.,2,180.,0 Variables: r1=1.41076711 r2=1.26224901 r3=1.1498688	O Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,0.,0 N,4,r3,5,90.,2,180.,0 Variables: r1=1.45442343 r2=1.65648671 r3=1.1497893
Be-*c*CNO (**6**)	NBeCO (**7**)	N-*c*BeOC (**8**)	NBeOC (**9**)
Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,0.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=3.62072445 r2=1.16367597 r3=1.29680248 a1=14.79936943 a2=183.12664288	N Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,180.,0 Variables: r1=1.521159 r2=1.66270268 r3=1.13702189	N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,a2,0 Variables: r1=1.56568639 r2=1.59404305 r3=1.21530834 a1=151.46823369 a2=78.06611987	N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,180.,0 Variables: r1=1.46476117 r2=1.58698443 r3=1.14695195
BeC-*c*NO (**11**)	BeNCO (**1q**)	BeOCN (**2q**)	BeONC (**3q**)
Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.7136954 r2=1.23774526 r3=1.60074365 a1=146.01811196 a2=56.41945836	Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.5397481 r2=1.36986943 r3=1.18527854 a1=142.17615301 a2=128.5165608	Be O,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,a2,0 Variables: r1=1.42350862 r2=1.29658625 r3=1.2846982 a1=168.84691375 a2=122.54896526	Be O,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,a2,0 Variables: r1=1.66334861 r2=1.43214509 r3=1.48264573 a1=62.19742121 a2=67.49607054
BeCNO (**4q**)	Be-*c*NCO (**5q**)	Be-*c*CNO (**6q**)	OBeNC (**7q**)
Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.62351086 r2=1.24665095 r3=1.24724529 a1=178.4055917 a2=125.88148308	Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.51049432 r2=1.29742089 r3=1.22188612 a1=185.38787305 a2=122.15041858	Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.64111081 r2=1.41047196 r3=1.42105255 a1=156.86985551 a2=57.88081571	O Be,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,180.,0 Variables: r1=1.48541583 r2=1.49998799 r3=1.2174237

OBeCN (**8q**)	N-*c*BeOC (**9q**)	NBeOC (**10q**)	NBeCO (**11q**)
O Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,180.,0 Variables: r1=1.47206153 r2=1.62443162 r3=1.2966569	N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,a2,0 Variables: r1=1.60236365 r2=1.59314404 r3=1.22328505 a1=145.58840087 a2=76.44086804	N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,180.,0 Variables: r1=1.60211663 r2=1.43161125 r3=1.26202903	N Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,180.,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,180.,0 Variables: r1=1.61057553 r2=1.62943463 r3=1.16915273
TS1 O Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,a2,0 Variables: r1=1.38878981 r2=1.64940083 r3=1.17822594 a1=69.47406891 a2=179.80403642	**TS2** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,0.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.75438739 r2=1.20478212 r3=1.23738728 a1=67.61513712 a2=146.77536673	**TS3** Be C,1,r1 X,2,1.,1,90. N,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,d1,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.71979923 r2=1.27601815 r3=1.98065516 a1=121.81821632 a2=40.64197279 d1=180.25234766	**TS4** N Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.45438086 r2=1.65238384 r3=1.1338031 a1=94.2849313 a2=189.14270709
TS6 Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,0.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.45163334 r2=2.7308922 r3=1.15640199 a1=55.94793437 a2=80.72865883	**TS7** O Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 N,4,r3,5,90.,2,a2,0 Variables: r1=1.4598733 r2=1.66609769 r3=1.1672892 a1=176.3990892 a2=90.92218249	**TS9** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,0.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.62910532 r2=1.19671208 r3=1.86625327 a1=75.76924733 a2=109.06165319	**TS10** Be N,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,d1,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.68929257 r2=1.19695646 r3=2.53324065 a1=189.67054803 a2=24.29240652 d1=-0.04185431
TS11 N Be,1,r1 X,2,1.,1,90. C,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 O,4,r3,5,90.,2,a2,0 Variables: r1=1.56732595 r2=1.77104424 r3=1.18376997 a1=181.76235526 a2=105.75705932	**TS12** N Be,1,r1 X,2,1.,1,90. O,2,r2,3,90.,1,a1,0 X,4,1.,2,90.,3,180.,0 C,4,r3,5,90.,2,a2,0 Variables: r1=1.49210214 r2=1.58560214 r3=1.20999394 a1=222.77153182 a2=83.86406236		

Table S4 Relative electronic energies (ΔE, in kcal mol^{-1}) with ZPVE correction, relative enthalpies (ΔH, in kcal mol^{-1}), and relative Gibbs free energies (ΔG, in kcal mol^{-1}) of the isomers, transition states, and dissociation fragments of the [Be,N,C,O] molecular system computed at different levels and the HOMO-LUMO gaps (HLGs, in eV) computed at the B2PLYPD3/6-311+G(2df).

Species	B3LYP-D3BJ/ 6-311+G(2df)			B2PLYPD3/ 6-311+G(2df)				M06-2X-D3/ *aug-cc-p*VQZ		
	ΔE	ΔH	ΔG	ΔE	ΔH	ΔG	HLGs	ΔE	ΔH	ΔG
1 ($C_{\infty V}$, $^2\Sigma$)	0.00	0.00	0.00	0.00	0.00	0.00	5.99	0.00	0.00	0.00
2 ($C_{\infty V}$, $^2\Pi$)	19.56	19.91	19.22	20.08	20.41	19.79	7.62	17.23	17.50	17.21
3a ($C_{\infty V}$, $^2\Sigma$)	23.41	23.70	22.35	/	/	/	--	20.08	19.21	21.36
3b (C_S, ^{2}A')	/	/	/	22.27	22.32	21.53	6.04	/	/	/
4 ($C_{\infty V}$, $^2\Pi$)	23.39	23.63	23.20	21.96	22.17	21.85	7.84	22.72	22.90	22.81
5 ($C_{\infty V}$, $^2\Sigma$)	83.54	83.52	83.71	82.31	82.28	82.54	6.12	/	/	/
6 (C_S, ^{2}A')	87.31	87.48	86.19	87.81	87.95	86.74	6.04	83.99	84.06	83.15
7 ($C_{\infty V}$, $^2\Pi$)	84.55	84.85	84.17	90.65	90.92	90.36	8.19	89.24	89.51	89.10
8 (C_S, ^{2}A")	101.99	102.20	100.58	106.19	106.33	104.91	9.01	101.40	101.49	100.36
9 ($C_{\infty V}$, $^2\Pi$)	105.24	105.68	104.82	113.54	114.08	112.85	5.71	109.53	110.01	109.25
10 (C_S, ^{2}A')	126.65	126.87	125.18	126.48	126.69	124.98	6.04	/	/	/
11 (C_S, ^{2}A')	126.68	126.71	125.52	125.40	125.30	124.36	6.12	128.21	128.16	127.37
1q (C_S, ^{4}A")	104.26	104.31	102.90	108.52	108.51	107.24	3.70	110.54	110.39	109.55
2q (C_S, ^{4}A')	107.08	107.38	104.95	110.62	110.94	108.33	4.90	111.06	111.27	109.34
3q (C_S, ^{4}A')	190.90	191.14	189.31	192.40	192.57	190.93	4.73	189.51	189.53	188.40
4q (C_S, ^{4}A')	143.19	143.30	141.60	148.61	148.69	147.08	4.87	151.37	151.39	150.09
5q (C_S, ^{4}A')	91.53	91.71	89.70	95.76	95.93	93.93	4.27	99.10	99.23	97.51
6q (C_S, ^{4}A')	157.72	157.64	156.29	160.10	160.00	158.74	5.50	159.54	159.36	158.47
7q ($C_{\infty V}$, $^4\Pi$)	137.76	138.21	136.85	140.86	141.25	140.08	1.71	155.88	155.92	155.54
8q ($C_{\infty V}$, $^4\Pi$)	137.49	137.97	136.29	142.26	142.70	141.16	2.97	142.95	143.45	141.00
9q (C_S, ^{4}A")	109.72	109.86	108.00	111.45	111.56	109.81	6.12	107.19	107.24	105.80
10q ($C_{\infty V}$, $^4\Pi$)	119.65	120.15	118.65	123.12	123.61	122.14	4.25	119.49	119.92	118.81
11q ($C_{\infty V}$, $^4\Pi$)	100.02	100.49	98.83	102.11	102.49	101.26	4.16	101.55	101.96	100.64
TS1	65.25	65.01	64.34	67.27	67.02	66.41	/	67.79	67.50	67.17
TS2	43.24	42.76	42.66	41.59	41.10	41.06	/	37.92	37.31	37.68
TS3	131.51	131.41	130.32	135.73	135.23	135.09	/	139.77	139.63	138.85
TS4	92.39	92.08	91.42	97.53	97.24	96.59	/	97.13	96.73	96.49
TS5	138.34	138.14	137.53	137.30	137.02	136.61	/	/	/	/
TS6	122.23	122.25	120.91	122.83	122.76	121.71	/	120.49	120.40	119.57
TS7	37.18	37.08	36.00	36.05	35.92	34.94	/	33.60	33.42	32.74
TS8	95.62	95.34	94.89	96.30	95.96	95.67	/	/	/	/
TS9	57.07	56.65	56.39	59.32	58.90	58.68	/	55.88	55.39	55.50
TS10	96.31	96.20	95.37	99.85	99.74	98.96	/	96.15	95.97	95.52
TS11	110.76	110.80	109.35	114.14	114.11	112.81	/	113.21	113.15	112.11
TS12	106.84	106.61	105.82	113.70	113.47	112.72	/	107.61	107.32	106.89
Be (^{1}S) + NCO ($^2\Pi$)	103.04	103.67	96.42	103.02	103.63	96.47	/	104.92	105.47	98.63
Be (^{1}S) + CNO ($^2\Pi$)	164.99	165.83	158.28	166.59	167.38	159.96	/	165.79	166.51	159.44
Be (^{3}P) + NCO ($^2\Pi$)	159.64	160.28	152.38	160.59	161.20	153.40	/	168.07	168.63	161.14
Be (^{3}P) + CNO ($^2\Pi$)	221.60	222.43	214.24	224.16	224.96	216.89	/	228.95	229.66	221.95
BeO ($^1\Sigma$) + CN ($^2\Sigma$)	135.24	136.23	126.32	129.91	130.88	121.04	/	137.06	137.98	128.48
BeO ($^3\Pi$) + CN ($^2\Sigma$)	154.79	155.79	145.10	153.35	154.33	143.72	/	155.79	156.72	146.43
BeN ($^2\Pi$) + CO ($^1\Sigma$)	127.82	128.82	118.80	128.70	129.67	119.73	/	127.65	128.59	118.95
BeN ($^4\Sigma$) + CO ($^1\Sigma$)	120.99	122.01	111.47	119.92	120.91	110.47	/	118.44	119.38	109.24
O (^{3}P) + BeNC ($^2\Sigma$)	140.14	141.29	132.07	139.67	140.81	131.66	/	139.06	140.19	131.21
O (^{3}P) + BeCN ($^2\Sigma$)	146.85	147.90	138.89	144.32	145.34	136.43	/	147.68	148.68	139.99

Table S5 Relative electronic energies (E, in kcal mol^{-1}) with ZPVE correction of the four low-lying isomers computed at various DFT and CCSD(T) levels for the [Be,N,C,O] molecular system. The ground electronic states and Be-O-C angles (θ, degree, in parentheses) are given for only BeOCN; other three isomers are linear with $^2\Sigma$ ground electronic states.

	BeNCO (**1**)	OBeNC (**2**)	BeOCN (**3a** or **3b**)	OBeCN (**4**)
B3LYP/6-311+G(d)	0.00	18.72	23.94 ($^2\Sigma$, 180.0)	21.98
B3LYP-D3(BJ)/6-311+G(d)	0.00	19.14	24.12 ($^2\Sigma$, 180.0)	22.59
B3LYP-D3(BJ)/6-311+G(2df)	0.00	19.56	23.41 ($^2\Sigma$, 180.0)	23.39
M06-2X/*cc-p*VTZ	0.00	16.79	20.27 ($^2\Sigma$, 180.0)	22.15
M06-2X/*cc-p*VQZ	0.00	17.23	20.14 ($^2\Sigma$, 180.0)	22.69
M06-2X/*aug-cc-p*VTZ	0.00	16.61	20.10 ($^2\Sigma$, 180.0)	22.04
M06-2X-D3/*aug-cc-p*VQZ	0.00	17.23	20.08 ($^2\Sigma$, 180.0)	22.72
M06-2X/*aug-cc-p*CVQZ	0.00	17.23	20.03 ($^2\Sigma$, 180.0)	22.77
PBE0/6-311+G(d)	0.00	26.07	25.58 ($^2\Sigma$, 180.0)	28.68
PBE0/*aug-cc-p*VQZ	0.00	26.08	24.37 ($^2\Sigma$, 180.0)	29.23
PBE0/*aug-cc-p*CVQZ	0.00	26.17	24.37 ($^2\Sigma$, 180.0)	29.31
B2PLYPD3/6-311+G(2df)	0.00	20.08	22.27 (^{2}A', 170.5)	21.96
DSD-PBEP86-D3(BJ)/6-311+G(d)	0.00	20.93	22.82 (^{2}A', 155.6)	21.84
DSD-PBEP86-D3(BJ)/*aug-cc-p*VTZ	0.00	21.75	21.77 (^{2}A', 155.6)	23.21
DSD-PBEP86-D3(BJ)/*aug-cc-p*VQZ	0.00	22.14	21.82 (^{2}A', 155.6)	23.71
DSD-PBEP86-D3(BJ)/*aug-cc-p*CVQZ	0.00	22.15	21.82 (^{2}A', 157.0)	23.72
*rev*DSD-PBEP86-D3(BJ)/6-311+G(d)	0.00	19.55	22.43 (^{2}A', 149.0)	20.50
*rev*DSD-PBEP86-D3(BJ)/*aug-cc-p*VTZ	0.00	20.23	21.39 (^{2}A', 155.7)	21.71
*rev*DSD-PBEP86-D3(BJ)/*aug-cc-p*VQZ	0.00	20.43	21.45 (^{2}A', 156.1)	22.19
*rev*DSD-PBEP86-D3(BJ)/*aug-cc-p*CVQZ	0.00	20.61	21.46 (^{2}A', 155.7)	22.20
*ω*B97XD/6-311+G(d)	0.00	22.15	24.57 (^{2}A', 163.4)	25.24
*ω*B97XD/*aug-cc-p*VQZ	0.00	22.41	23.70 (^{2}A', 158.1)	25.86
*ω*B97XD/*aug-cc-p*CVQZ	0.00	22.52	23.68 (^{2}A', 158.1)	25.94
CCSD(T)/*cc-p*VTZ	0.00	15.68	19.75 (^{2}A', 148.3)	17.84
CCSD(T)/*cc-p*VQZ	0.00	16.70	19.80 (^{2}A', 153.0)	19.07
CCSD(T)/*aug-cc-p*VTZ	0.00	15.95	19.63 (^{2}A', 150.6)	18.26
CCSD(T)/*aug-cc-p*VQZ	0.00	16.81	19.80 (^{2}A', 153.0)	19.29

Table S6 Valent molecular orbitals (VMOs) and the number of occupied electron (in parentheses), the contribution ((Cont., %)) of an atomic orbital (AO) to a MO, total contribution (TC) and composition proportion (CP) of all AOs of one atom to a MO, and orbital delocalization indices (ODI) computed at the CCSD(T)/*aug-cc-p*VQZ level of theory for BeNCO.

VMOs	Atom	AOs	Cont.	TC	CP	ODI	VMOs	Atom	AOs	Cont.	TC	CP	ODI
5α(1)	C	2s	15.93	18.78	$sp^{0.18}$	68.25	5β(1)	C	2s	15.80	18.64	$sp^{0.18}$	68.45
		$2p_z$	2.85						$2p_z$	2.84			
	O	2s	77.88	81.22	$sp^{0.04}$			O	2s	78.04	81.36	$sp^{0.04}$	
		$2p_z$	3.34						$2p_z$	3.32			
6α(1)	N	2s	71.13	74.51	$sp^{0.05}$	58.93	6β(1)	N	2s	70.45	74.11	$sp^{0.05}$	58.53
		$2p_z$	3.38						$2p_z$	3.66			
	C	2s	12.59	21.48	$sp^{0.71}$			C	2s	12.84	21.82	$sp^{0.70}$	
		$2p_z$	8.89						$2p_z$	8.98			
	O	2s	4.02	4.02				O	2s	4.06	4.06		
7α(1)	Be	2s	5.77	7.38	$sp^{0.28}$	30.96	7β(1)	Be	2s	4.65	6.24	$sp^{0.34}$	30.22
		$2p_z$	1.61						$2p_z$	1.59			
	N	2s	22.58	43.09	$sp^{0.91}$			N	2s	21.16	38.11	$sp^{0.80}$	
		$2p_z$	20.51						$2p_z$	16.95			
	C	2s	24.03	24.03				C	2s	24.44	24.44		
	O	2s	13.40	25.51	$sp^{0.90}$			O	2s	15.84	31.21	$sp^{0.97}$	
		$2p_z$	12.11						$2p_z$	15.37			
8α(1)	Be	2s	2.47	3.61	$sp^{0.46}$	43.60	8β(1)	Be	2s	2.93	4.60	$sp^{0.57}$	39.06
		$2p_z$	1.14						$2p_z$	1.67			
	N	2s	2.47	18.47	$sp^{6.48}$			N	2s	3.68	23.07	$sp^{5.27}$	
		$2p_z$	16.00						$2p_z$	19.39			
	C	2s	1.36	15.13	$sp^{10.14}$			C	2s	0.68	15.14	$sp^{21.19}$	
		$2p_z$	13.77						$2p_z$	14.46			
	O	2s	23.42	62.80	$sp^{1.68}$			O	2s	20.83	57.19	$sp^{1.75}$	
		$2p_z$	39.38						$2p_z$	36.36			
9α(1)	N	$2p_y$	16.70	16.70		41.81	9β(1)	N	$2p_y$	16.50	16.50		42.14
	C	$2p_y$	26.63	26.63				C	$2p_y$	26.41	26.41		
	O	$2p_y$	56.67	56.67				O	$2p_y$	57.09	57.09		
10α(1)	N	$2p_x$	16.70	16.70		41.81	10β(1)	N	$2p_x$	16.50	16.50		42.14
	C	$2p_x$	26.63	26.63				C	$2p_x$	26.41	26.41		
	O	$2p_x$	56.67	56.67				O	$2p_x$	57.09	57.09		
11α(1)	Be	$2p_y$	1.02	1.02		48.23	11β(1)	Be	$2p_y$	0.73	0.73		48.47
	N	$2p_y$	59.64	59.64				N	$2p_y$	59.61	59.61		
	C	$2p_y$	1.36	1.36				C	$2p_y$	1.59	1.59		
	O	$2p_y$	37.98	37.98				O	$2p_y$	38.07	38.07		
12α(1)	Be	$2p_x$	1.02	1.02		48.23	12β(1)	Be	$2p_x$	0.73	0.73		48.47
	N	$2p_x$	59.64	59.64				N	$2p_x$	59.61	59.61		
	C	$2p_x$	1.36	1.36				C	$2p_x$	1.59	1.59		
	O	$2p_x$	37.98	37.98				O	$2p_x$	38.07	38.07		
13α(1)	Be	2s	67.18	97.20	$sp^{0.45}$	91.11	13β(0)	Be	2s	91.25	94.90	$sp^{0.04}$	87.20
		$2p_z$	30.02						$2p_z$	3.64			
	N	2s	1.78	1.78				N	2s	1.34	2.56	$sp^{0.90}$	
	C	2s	1.02	1.02					$2p_z$	1.21			
								C	2s	1.61	2.55	$sp^{0.58}$	
									$2p_z$	0.93			
14α(0)	Be	$2p_x$	90.51	90.51		77.81	14β(0)	Be	$2p_x$	94.95	94.95		86.12
	N	$2p_x$	1.12	1.12				C	$2p_x$	3.37	3.37		
	C	$2p_x$	5.47	5.47				O	$2p_x$	1.68	1.68		
	O	$2p_x$	2.90	2.90									

Table S7 Valent molecular orbitals (VMOs) and the number of occupied electron (in parentheses), the contribution ((Cont., %)) of an atomic orbital (AO) to a MO, total contribution (TC) and composition proportion (CP) of all AOs of one atom to a MO, and orbital delocalization indices (ODI) computed at the CCSD(T)/*aug-cc-p*VQZ level of theory for OBeNC.

VMOs	Atom	AOs	Cont.	TC	CP	ODI	VMOs	Atom	AOs	Cont.	TC	CP	ODI
5α(1)	O	2s	99.40	99.40		95.27	6β(1)	O	2s	97.59	97.59		92.38
	Be	2s	0.60	0.60				Be	2s	1.71	2.41	$sp^{0.41}$	
									$2p_z$	0.70			
6α(1)	N	2s	72.85	76.17	$sp^{0.05}$	62.76	5β(1)	N	2s	72.92	76.12	$sp^{0.05}$	62.78
		$2p_z$	3.32						$2p_z$	3.30			
	C	2s	18.83	23.83	$sp^{0.27}$			C	2s	18.79	23.78	$sp^{0.27}$	
		$2p_z$	5.00						$2p_z$	5.00			
7α(1)	Be	2s	8.42	12.22	$sp^{0.45}$	47.51	7β(1)	Be	2s	8.49	12.28	$sp^{0.45}$	47.48
		$2p_z$	3.80						$2p_z$	3.79			
	N	2s	24.82	63.96	$sp^{1.58}$			N	2s	24.76	63.93	$sp^{1.58}$	
		$2p_z$	39.14						$2p_z$	39.17			
	C	2s	23.12	23.82	$sp^{0.03}$			C	2s	23.10	23.80	$sp^{0.03}$	
		$2p_z$	0.70						$2p_z$	0.70			
8α(1)	O	$2p_y$	99.21	99.21		96.79	10α(1)	O	$2p_x$	95.91	95.91		88.97
	Be	$2p_y$	0.79	0.79				Be	$2p_x$	2.04	2.04		
								N	$2p_x$	2.05	2.05		
9α(1)	O	2s	7.50	82.29	$sp^{9.98}$	68.93	8β(1)	O	2s	9.34	79.80	$sp^{7.54}$	65.82
		$2p_z$	74.79						$2p_z$	70.46			
	Be	2s	12.71	15.95	$sp^{0.25}$			Be	2s	14.31	17.45	$sp^{0.22}$	
		$2p_z$	3.24						$2p_z$	3.14			
	N	2s	1.04	1.77	$sp^{0.70}$			N	2s	0.76	1.94	$sp^{1.56}$	
		$2p_z$	0.73						$2p_z$	1.18			
								C	2s	0.82	0.82		
9β(1)	O	$2p_x$	46.12	46.12		38.04	11β(1)	O	$2p_x$	61.36	61.36		46.53
	Be	$2p_x$	3.16	3.16				N	$2p_x$	30.03	30.03		
	N	$2p_x$	40.07	40.07				C	$2p_x$	8.61	8.61		
	C	$2p_x$	10.64	10.64									
11α(1)	O	$2p_y$	0.51	0.51		63.16	10β(1)	Be	$2p_y$	0.80	0.80		64.47
	Be	$2p_y$	0.61	0.61				N	$2p_y$	78.20	78.20		
	N	$2p_y$	77.66	77.66				C	$2p_y$	21.01	21.01		
	C	$2p_y$	21.22	21.22									
12α(1)	O	$2p_x$	7.54	7.54		56.16	13β(0)	O	$2p_y$	23.30	23.30		51.45
	N	$2p_x$	72.46	72.46				Be	$2p_y$	67.90	67.90		
	C	$2p_x$	20.01	20.01				C	$2p_y$	8.81	8.81		
13α(1)	N	2s	1.32	9.79	$sp^{6.44}$	79.25	12β(1)	N	2s	1.32	9.80	$sp^{6.44}$	79.23
		$2p_z$	8.47						$2p_z$	8.48			
	C	2s	64.08	90.21	$sp^{0.41}$			C	2s	64.11	90.20	$sp^{0.41}$	
		$2p_z$	26.13						$2p_z$	26.09			
14α(0)	O	2s	4.70	5.72	$sp^{0.22}$	64.96	14β(0)	O	2s	4.62	5.61	$sp^{0.21}$	64.53
		$2p_z$	1.02						$2p_z$	0.99			
	Be	2s	79.12	79.12				Be	2s	78.80	78.80		
	N	2s	11.99	14.04	$sp^{0.17}$			N	2s	12.35	14.41	$sp^{0.17}$	
		$2p_z$	2.05						$2p_z$	2.06			
	C	2s	1.12	1.12				C	2s	1.19	1.19		

Table S8 Local topological properties (in a.u.) of the electronic charge density distribution at bond critical points (BCPs) and bond delocalization indices (BDI), computed at the CCSD(T)/*aug-cc-p*VQZ level of theory, of BeNCO and OBeNC.

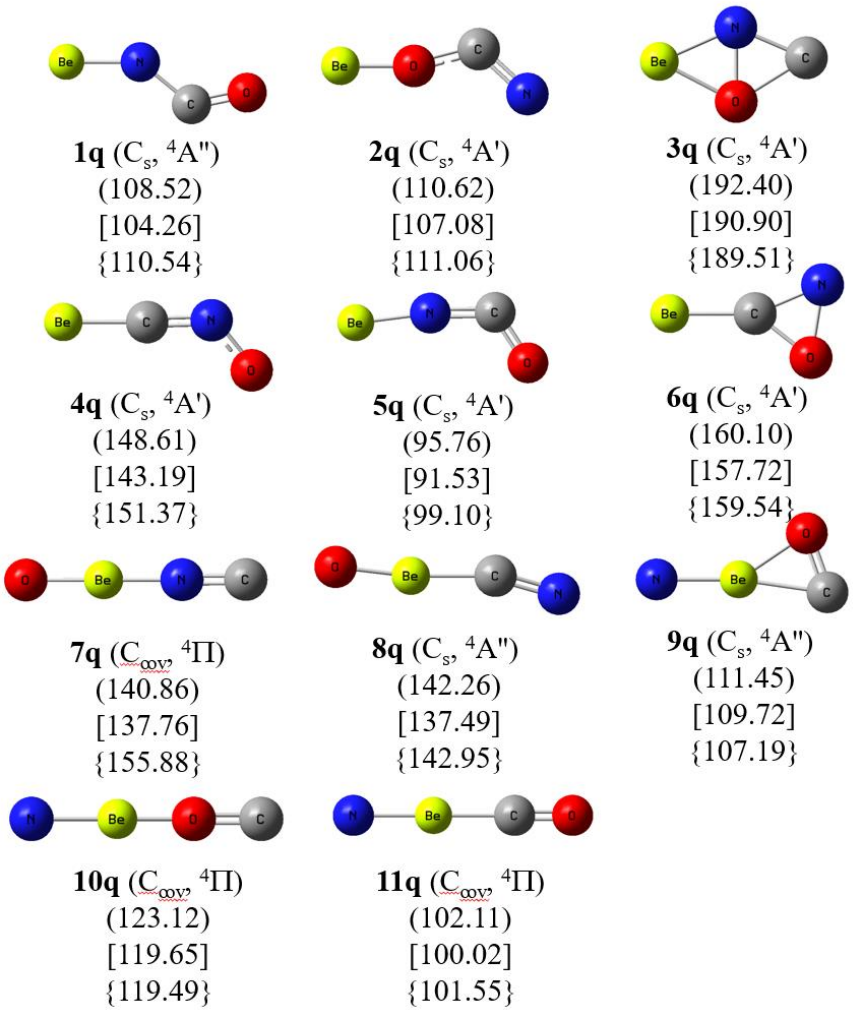
Species	Bond	BDI	$\rho(\mathbf{r}_c)$	$\nabla^2\rho(\mathbf{r}_c)$	$V(\mathbf{r}_c)$	$G(\mathbf{r}_c)$	$\lvert V(\mathbf{r}_c)\rvert/G(\mathbf{r}_c)$	$H(\mathbf{r}_c)$
BeNCO	Be-N	0.412	0.121	0.792	-0.259	0.229	1.134	-0.031
	N-C	1.324	0.453	-0.993	-1.557	0.654	2.379	-0.902
	C-O	1.091	0.475	0.140	-1.896	0.965	1.964	-0.930
OBeNC	O-Be	0.242	0.134	0.942	-0.307	0.271	1.132	-0.036
	Be-N	0.213	0.116	0.704	-0.237	0.206	1.147	-0.030
	N-C	1.722	0.475	-0.553	-1.794	0.828	2.167	-0.966

$\rho(r)$, electronic charge density; $\nabla^2\rho(r)$, Laplacian function of electronic density, $|V(r)|/G(r)$, relationship between the potential energy density $V(r)$ and the Lagrangian form of kinetic energy density $G(r)$, define as energies density of the unit of electrons; and $H(r)$, total energy density, define as $V(r) + G(r)$. $\mathbf{r}_c$ refers to the position at bond critical point.

Table S9 CCSD/*aug-cc-p*CVTZ-computed vibrational spectra of BeNCO and OBeNC using ^{13}C, ^{15}N, and ^{18}O isotopes.

	^{13}C		^{15}N		^{18}O		
	ν [a] or C [b]	I [c]	ν [a] or C [b]	I [c]	ν [a] or C [b]	I [c]	mode [d]
BeNCO	104.0	0.6	102.2	0.6	103.4	0.6	BeNC (δ)
	104.0	0.6	102.2	0.6	103.4	0.6	BeNC (δ)
	636.8	22.4	652.5	23.3	650.0	23.0	NCO (δ)
	636.8	22.4	652.5	23.3	650.0	23.0	NCO (δ)
	889.4	149.7	890.2	152.2	878.9	147.8	Be-N-(CO) symm stretch
	1540.6	88.6	1516.0	106.2	1514.7	90.1	NCO sym stretch
	2260.4	1748.9	2309.5	1765.0	2307.2	1800.8	NCO asym stretch
	2419.8	17.3	2397.0	41.9	2384.2	50.6	$\nu_5 + \nu_6$
	3145.3	14.5	3194.7	14.9	3180.8	17.0	$\nu_5 + \nu_7$
	3785.5	16.9	3809.8	19.0	3806.4	17.4	$\nu_6 + \nu_7$
OBeNC	156.4	2.7	154.3	2.8	155.8	3.3	BeNC (δ)
	156.4	2.7	154.3	2.8	155.8	3.3	BeNC (δ)
	391.2	106.4	389.4	106.0	387.7	104.8	OBeN (δ)
	391.2	106.3	389.4	106.0	387.7	104.8	OBeN (δ)
	565.2	2.3	565.0	1.9	552.7	3.1	OBeN sym stretch
	1255.3	535.7	1257.9	547.2	1251.1	535.8	O-Be-NC asym stretch
	2117.4	392.9	2119.6	368.4	2156.0	386.3	OBe-N-C asym stretch

[a] anharmonic frequencies of fundamental modes (cm^{-1}); [b] combination bands of fundamental modes (cm^{-1}); [c] anharmonic vibrational intensities (km mol^{-1}); [d] assignment of vibrational modes, δ: scissoring vibration.



1q (C_s, ^{4}A'')
(108.52)
[104.26]
{110.54}

2q (C_s, ^{4}A')
(110.62)
[107.08]
{111.06}

3q (C_s, ^{4}A')
(192.40)
[190.90]
{189.51}

4q (C_s, ^{4}A')
(148.61)
[143.19]
{151.37}

5q (C_s, ^{4}A')
(95.76)
[91.53]
{99.10}

6q (C_s, ^{4}A')
(160.10)
[157.72]
{159.54}

7q ($C_{\infty v}$, $^4\Pi$)
(140.86)
[137.76]
{155.88}

8q (C_s, ^{4}A'')
(142.26)
[137.49]
{142.95}

9q (C_s, ^{4}A'')
(111.45)
[109.72]
{107.19}

10q ($C_{\infty v}$, $^4\Pi$)
(123.12)
[119.65]
{119.49}

11q ($C_{\infty v}$, $^4\Pi$)
(102.11)
[100.02]
{101.55}

Fig. S1 Schematic structures and relative electronic energies (REs) with ZPVE correction of the isomers optimized at the B2PLYPD3/6-311+G(2df) (REs in parentheses), B3LYP-D3BJ/6-311+G(2df) (REs in square brackets), and M06-2X-D3/*aug-cc-p*VQZ (REs in curly brackets) levels of theory for the [Be,N,C,O] isomers in electronic quartet.

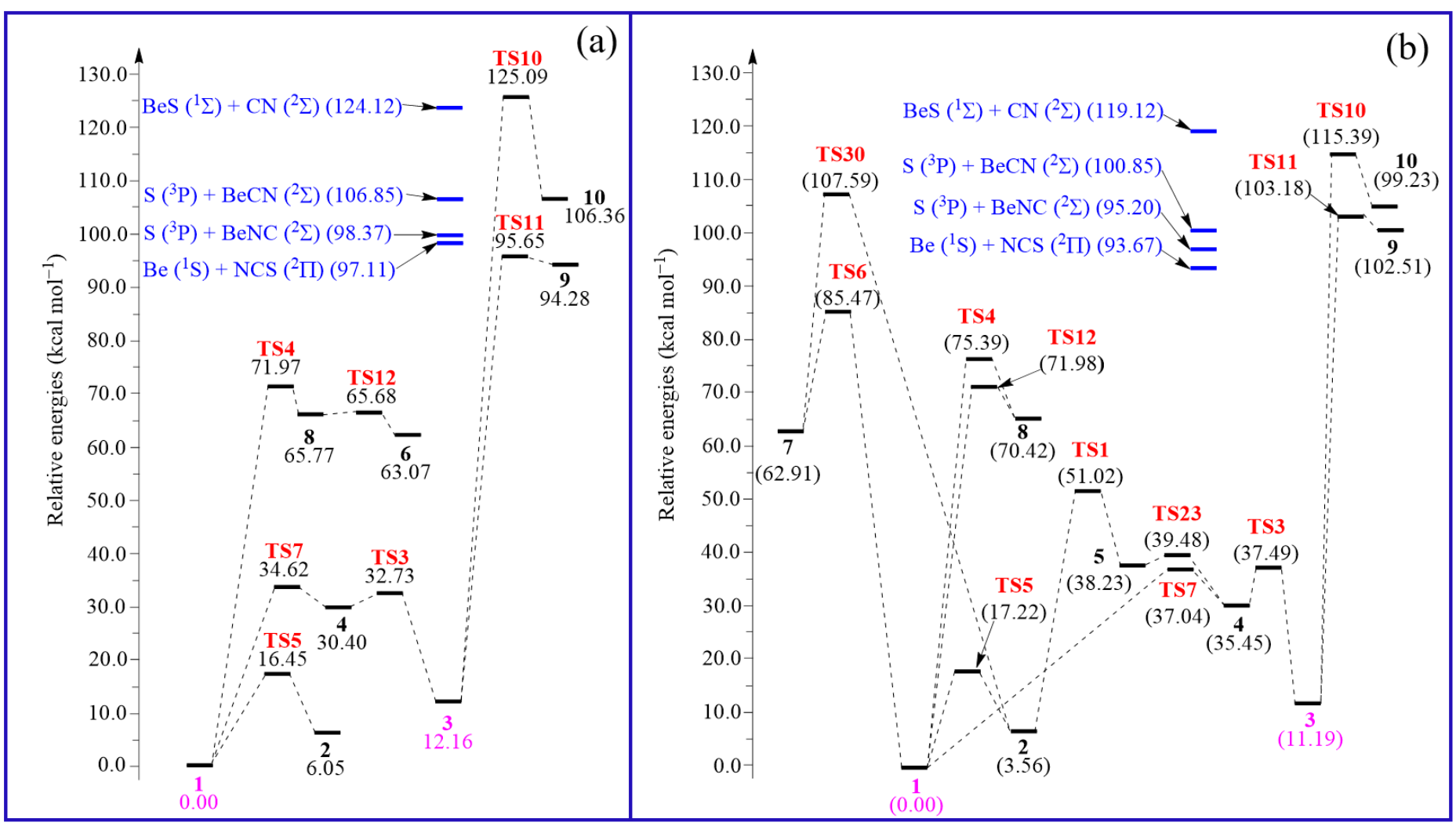
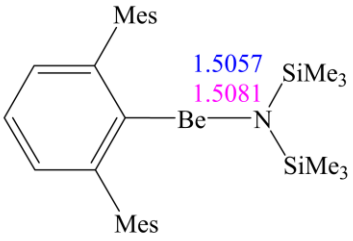
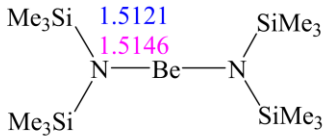


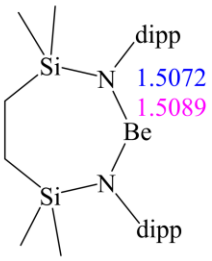
Fig. S2 Isomerization reaction potential energy profiles of the [Be,N,C,O] system constructed at the B3LYP-D3BJ/6-311+G(2df) (a) and M06-2X-D3/*aug-cc-p*VQZ (b) levels of theory.



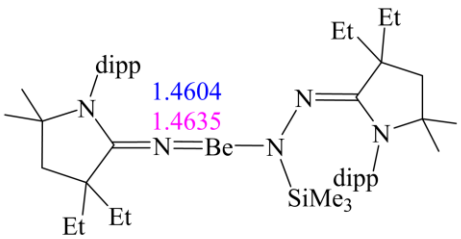
(2,6-$Mes_2C_6H_3$)BeN($SiMe_3$)$_2$ (**I**)



Be[N($SiMe_3$)$_2$]$_2$) (**II**)

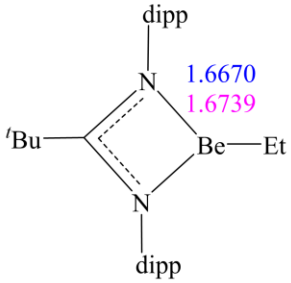


BeN(dipp)Si(Me_2)CH=CHSi(Me_2)N(dipp) (**III**)

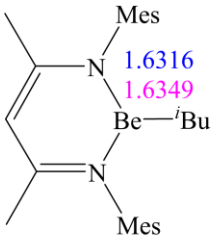


R = 1-dipp-3,3-diethyl-5,5-dimethylpyrrolidin-2-ylidene)

RNBeN($SiMe_3$)NR (**IV**)

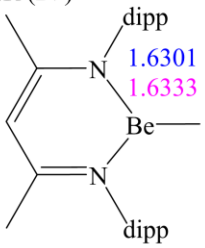


[^{t}BuC(N-dipp)$_2$]BeEt (**V**)



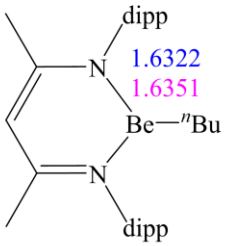
[HC(CMeNR^1)$_2$]Be(R^2) (**VI**)

R^1 = Mes, R^2 = ^{i}Bu



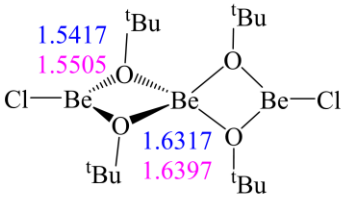
[HC(CMeNR^1)$_2$]Be(R^2) (**VII**)

R^1 = dipp, R^2 = Me

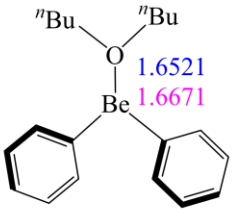


[HC(CMeNR^1)$_2$]Be(R^2) (**VIII**)

R^1 = dipp, R^2 = ^{n}Bu



$Be_3Cl_2(C_4H_9O)_4$ (**IX**)



(^{n}Bu)$_2$OBe(Ph)$_2$ (**X**)

Fig. S3 Schematic structures of some model compounds. The bond lengths (Å) optimized at the B3LYP-D3BJ/6-311++G(2df,2p) and B3LYP-D3BJ/6-311++G(d,p) are shown in blue and magenta, respectively.

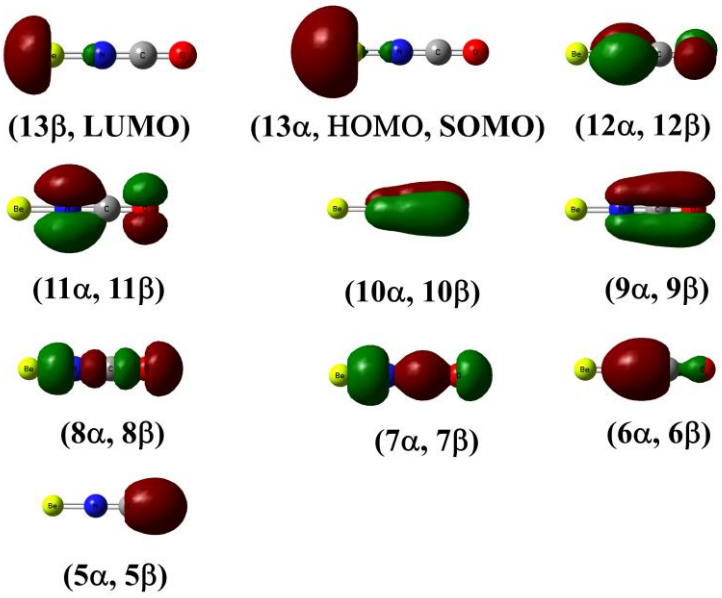


Fig. S4 Valent molecular orbitals (isovalue = 0.06), computed at the CCSD(T)/*aug-cc-p*VQZ level of theory, of BeNCO.

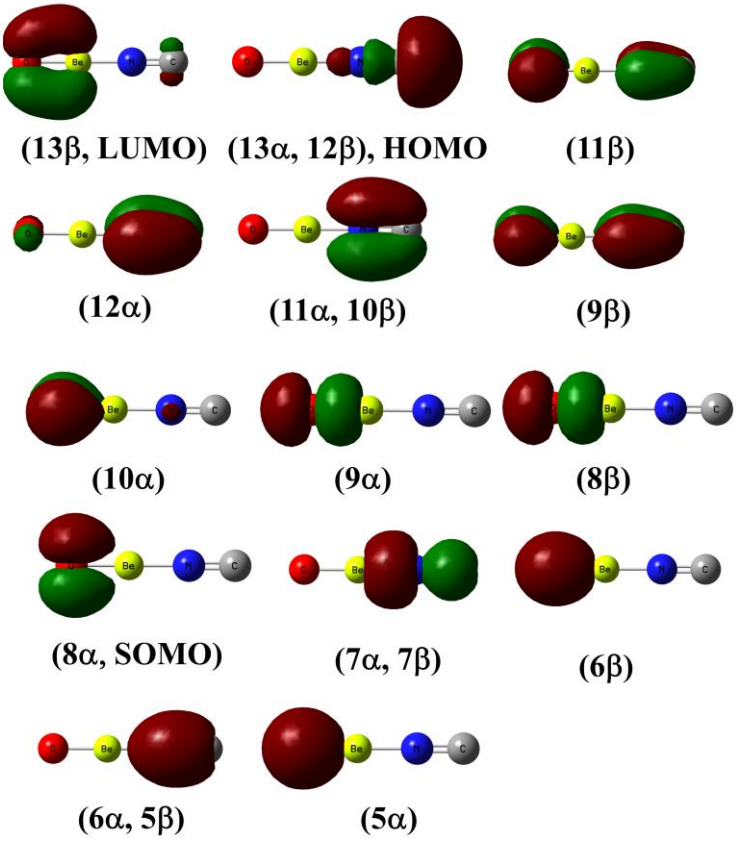


Fig. S5 Valent molecular orbitals (isovalue = 0.06), computed at the CCSD(T)/*aug-cc-p*VQZ level of theory, of OBeNC.

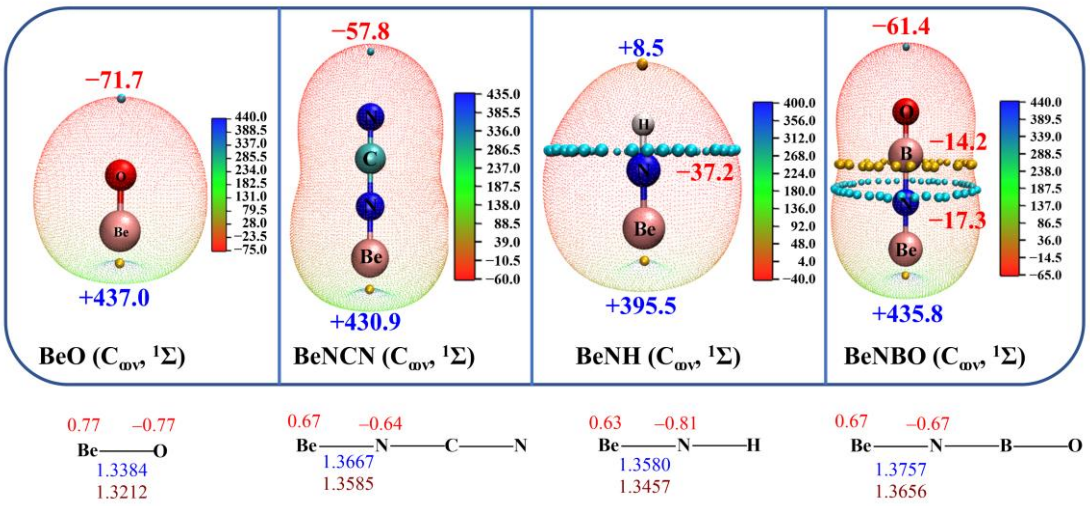


Fig. S6 Electrostatic potential plots and Mulliken charges (|e|, in red), computed at the CCSD(T)/*cc-p*VQZ level of theory, of four model molecules. The bond distances in blue and wine were optimized at the CCSD(T)/*aug-cc-p*VQZ and B3LYP-D3BJ/6-311+G(2df) levels of theory, respectively.

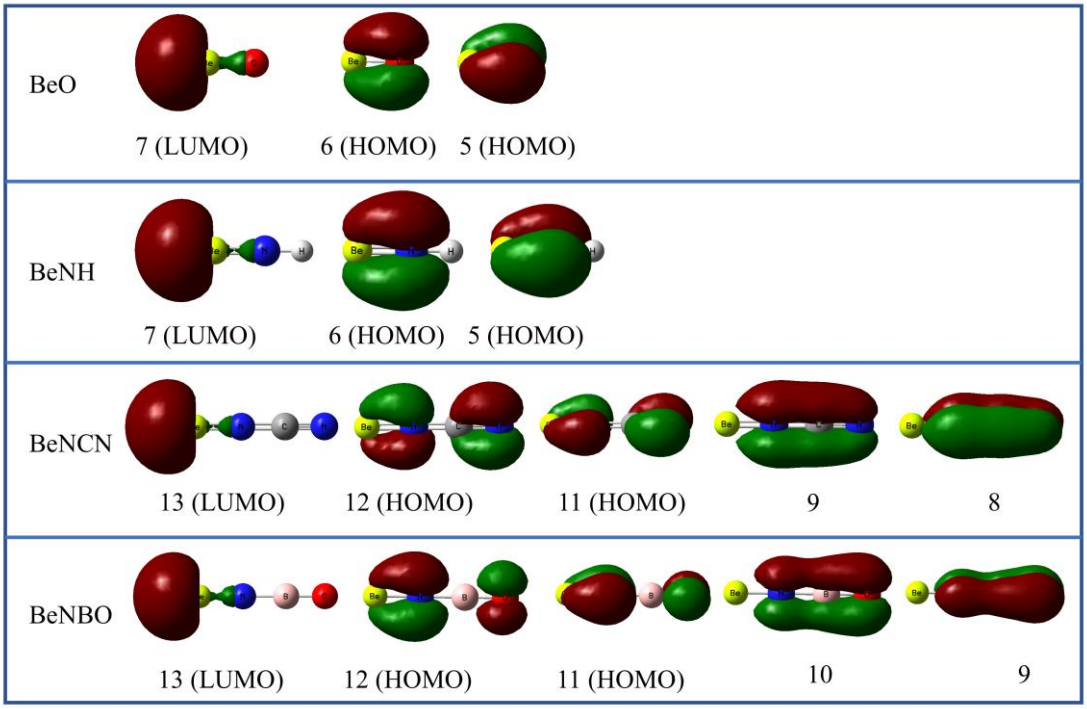


Fig. S7 Valent molecular orbitals (isovalue = 0.06), computed at the CCSD(T)/*cc-p*VQZ level of theory, of four model molecules.