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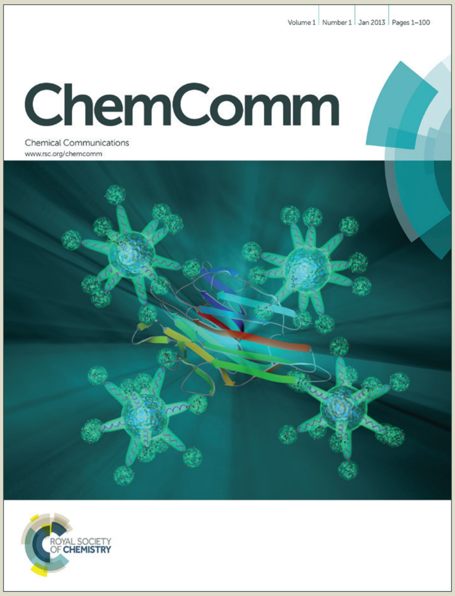

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# All the *2p*-block elements in a molecule: experimental and theoretical study of FBNCO and FBNCO$^+$.

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**Abstract. The new radical FBNCO and the new cation FBNCO$^+$, containing all the 2p-block elements, have been detected in the gaseous isolated state. Theoretical calculations predict that these species are very stable toward the dissociation.**

Following the Bartlett's early study of the structure and properties of 28-electron tetratomic molecules, [1] some elusive species such as $N_4$, [2] $BNO_2$ [3] and $N_2CO$ [4] have been experimentally detected by mass spectrometric experiments [2, 4] and matrix isolation infrared spectroscopy. [3] Others, such as for example $BFN_2$, $B_2F_2$ and BFCO, still wait for experimental observations. In some cases, the first experimental evidence of these species was successfully followed by the observation or synthesis of other isomers, as viable observable entities, [5] for instance diazirinone $N_2CO$ has been found to have a quite surprisingly half-life of 1.4 h at ambient temperature. [4] The $BNO_2$ species was assigned the OBON structure, and other simple molecules and radicals containing NBO or BNO groups were prepared in the same experiments. [3] Species containing the BN kernel are of great interest as building blocks of atomic layers and nanofilms, analogues to the most popular carbon nanotubes containing the isoelectronic CC group. [6] In this field, special attention is given to hybrid BNC films relevant to materials with tunable electronic properties, from insulating to conducting, depending on the carbon concentration. [6] While few-atoms species containing either B, N, O or B, C, O atoms have been experimentally detected, [3, 7] to the best of our knowledge, very little is known on simple radicals and molecules containing the BNC group. Early theoretical studies predicted the stability of structures having HBNC chains, with three-coordinate boron atoms; [8] HBNC was then observed as a minor product of the reaction of laser-ablated boron atoms with HCN. [9] FBNC chains can be found in $F_2BNCO$ and $FB(NCO)_2$, where boron is three-coordinate. [9]

In this work we report the first experimental evidence for the intriguing radical FBNCO, a 35-electron species containing all the 2p-block elements. The mass spectrometric technique adopted requires that a precursor ion is preliminarily built, thus, the hitherto unknown FBNCO$^+$ ions also have been prepared and detected for the first time.

The synthesis exploits an ion-molecule reaction (IMR) between $BF_2^+$ and isocyanic acid HNCO. The latter has been prepared according to established procedures, [10] and $BF_2^+$ is the most abundant ion obtained by ionization of $BF_3$ in the gas phase. The reaction occurs through a reaction intermediate [$BF_2^+$ -- HNCO], that yields [B, C, N, O, F]$^+$ ions by HF loss. The $B_2F_5^+$ ions also give this adduct by ligand exchange between $BF_3$ and HNCO, as observed with other nitrogen bases. [11]

$$BF_2^+ + HNCO \rightarrow [BF_2\text{-}HNCO]^+ \rightarrow [B,C,N,O,F]^+ + HF \qquad (1)$$

The reaction sequence has been identified through mass spectrometric experiments performed by different equipment. First, the [$^{11}BF_2$ -- HNCO]$^+$ adduct has been prepared and assayed by energy-resolved collisionally activated dissociation (CAD) (Figure 1A). At collision energies higher than 4 eV center of mass (CM), the spectrum is dominated by the loss of the HNCO molecule leading back to the $^{11}BF_2^+$ fragment. However, at the minimum collision energy required to the loss of the HNCO moiety, ca. 0.5 eV, the [$^{11}$B, C, N, O, F]$^+$ ion is also formed by HF loss. Secondly, the [$^{11}BF_2$ -- HNCO]$^+$ and [$^{10}BF_2$ -- HNCO]$^+$ adducts have been prepared under the same experimental conditions employed to detect the radical, then mass-selected and assayed by CAD. They both gave intense fragments at m/z 72 and 71 corresponding to the [$^{11}$B, C, N, O, F]$^+$ and [$^{10}$B, C, N, O, F]$^+$ ions, respectively (Figure 1B).

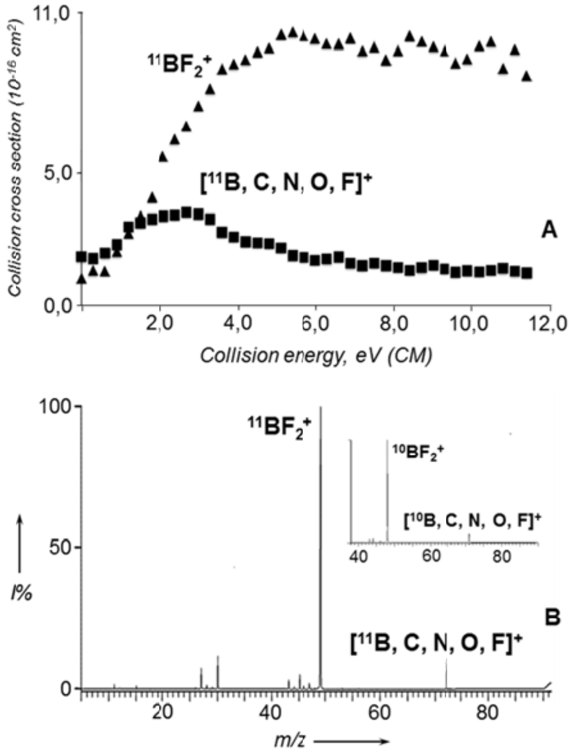


**Figure 1.** (A) Energy resolved TQ/CAD spectrum of [$^{11}BF_2$-HNCO]$^+$ ions. (B) CAD-TOF spectrum of [$^{11}BF_2$-HNCO]$^+$ and [$^{10}BF_2$-HNCO]$^+$ ions (0,8 keV accelerating voltage). See Supporting Information.

The assignment of the connectivity of the so-formed [B, C, N, O, F]$^+$ ions has been established by high-energy CAD and multi-stage mass spectrometry. The most intense fragments, i.e. FBN$^+$ and FB$^+$, the minor fragment BN$^+$ and the absence of the NF$^+$ fragment give strong evidence for the FBN kernel (Figure 2A). Other diagnostic fragments are CO$^+$, the small BNC$^+$ and CN$^+$ peaks, and those corresponding to the loss of the terminal atoms - fluorine or oxygen; the observed pattern thus allows the assignment of the FBNCO$^+$ connectivity. Notably, the minor peak at m/z 46, corresponding to the FBO$^+$ fragment, hints at a low fraction of FBOCN$^+$ ions. The reaction of formation of FBOCN$^+$ from $BF_2^+$ is computed to be endothermic by 38.9 kcal mol$^{-1}$ (Table 1), and the most likely route is the reaction (2) much less endothermic and accessible to BF$^+$ ions having a small excess of energy.

$$BF^+ + HNCO \rightarrow FBOCN^+ + H \qquad (2)$$

Consistent with this, the theoretical calculations have identified two linear isomers on the [B, C, N, O, F]$^+$ potential energy surface (PES), having FBNCO (**1**$^+$) and FBOCN (**2**$^+$) connectivity, respectively (Figure 3).[12] The latter is significantly higher in energy than the former, however they are both very stable with respect to the dissociation: the lowest energy dissociations, leading to BF$^+$ and FBO$^+$, are 161.3 and 111.7 kcal mol$^{-1}$, respectively (Table 1). Importantly, no isomerization path has been found between the two isomers **1**$^+$ and **2**$^+$. Isomers located at much higher energy are reported in the Supporting Information.

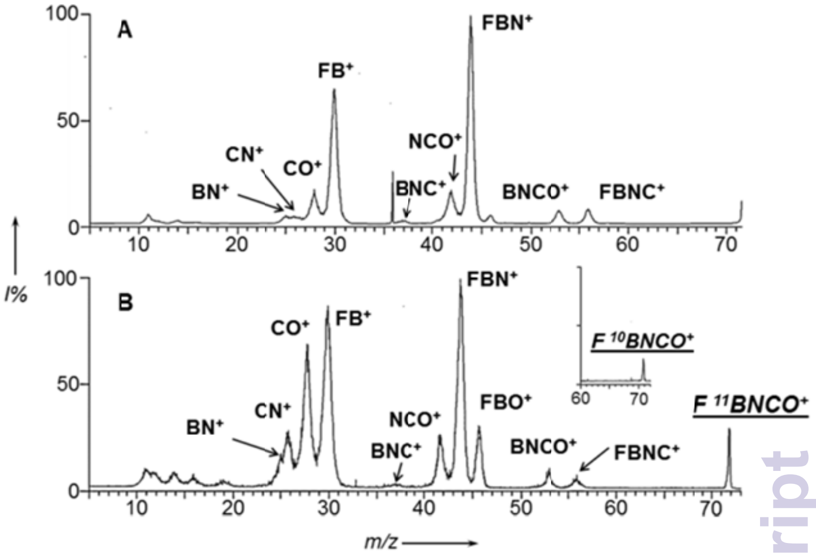


**Figure 2.** (A) CAD spectrum of F$^{11}$BNCO$^+$ ions (m/z 72, 8 keV accelerating voltage). Note the narrow doubly charged ion at m/z 36. (B) NR spectrum showing the "recovery peaks" at m/z 72 and 71 (in the inset), from the reionization of the F$^{11}$BNCO and F$^{10}$BNCO radicals.

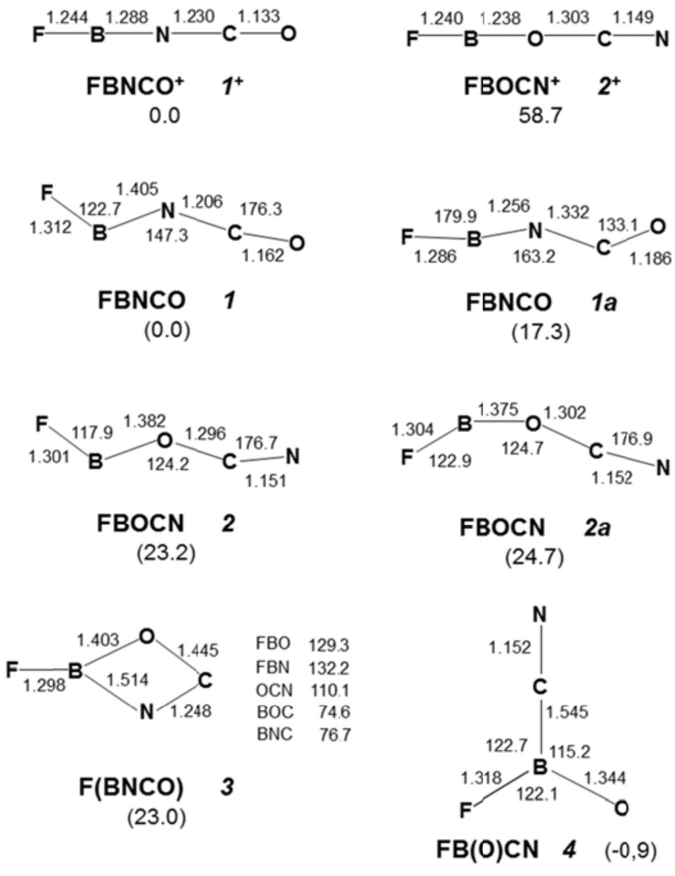


**Figure 3.** Geometries of the minima located on the [B, C, N, O, F]$^+$ and [B, C, N, O, F] potential energy surfaces optimized at the B3LYP/aug-cc-pVTZ level of theory. Bond lengths in Å and angles in degrees. *ΔH* values (kcal mol$^{-1}$) computed at CCSD(T)/aug-cc-pVTZ level of theory, relative to **1**$^+$ and **1**.

**Table 1.** Energy changes (kcal mol$^{-1}$, 298 K) for selected dissociation and isomerization reactions, computed at the CCSD(T) level of theory on B3LYP optimized geometries using the aug-cc-pVTZ basis set.

| | ΔH° | Barrier height |
|---|---|---|
| $BF_2^+$ + HNCO → $FBNCO^+$ ($^1\Sigma$) + HF | -19.7 | |
| $BF_2^+$ + HNCO → $FBOCN^+$ ($^1\Sigma$) + HF | 39.0 | |
| $BF^+$ + HNCO → $FBOCN^+$ ($^1\Sigma$) + H | 7.4 | |
| $FBNCO^+$ ($^1\Sigma$) → $FBN^+$ + CO | 162.1 | |
| $FBNCO^+$ ($^1\Sigma$) → $BF^+$ + NCO | 161.3 | |
| $FBNCO^+$ ($^1\Sigma$) → BF + $NCO^+$ ($^1$A') | 208.4 | |
| $FBNCO^+$ ($^1\Sigma$) → BF + $NCO^+$ ($^3$A") | 176.0 | |
| $FBOCN^+$ ($^1\Sigma$) → $FBO^+$ + CN | 111.7 | |
| $FBOCN^+$ ($^1\Sigma$) → FBO + $CN^+$ | 127.0 | |
| FBNCO ($^2$A') **(1)** → FBN + CO | 50.2 | |
| FBNCO ($^2$A') **(1)** → BF + NCO | 76.5 | |
| FBOCN ($^2$A') **(2)** → FBO + CN | 17.8 | |
| FBNCO ($^2$A') **(1)** → FBNCO ($^2$A) **(1a)** | 17.3 | 21.0 |
| FBNCO ($^2$A) **(1a)** → F(BOCN) ($^2$A) **(3)** | 5.7 | 19.1 |
| F(BOCN) ($^2$A) **(3)** → FBOCN ($^2$A') **(2)** | 0.2 | 30.1 |
| FBOCN ($^2$A') **(2)** → FBOCN ($^2$A') **(2a)** | 1.5 | 6.6 |
| FBOCN ($^2$A') **(2)** → FB(O)CN ($^2$A') **(4)** | - 24.1 | 15.5 |

The F$^{11}$BNCO$^+$ and F$^{10}$BNCO$^+$ ions have been submitted to neutralization by a vertical charge-transfer process that occurs in the femtosecond time scale; the process is then followed by vertical reionization which allows detection of a signal only if intact neutral species survive. The NR (neutralization-reionization) spectra of F$^{11}$BNCO$^+$ and F$^{10}$BNCO$^+$ ions show recovery peaks at m/z 72 and 71 (Figure 2B) that prove detection of the corresponding radical. The time elapsed from neutralization to reionization, under the employed experimental conditions, is 0.8 μs which is therefore the minimum lifetime that can be assigned to the radical detected. In such case, the vertical nature of the processes implies that the precursor ion, the neutral and the reionized species have the same structure, unless isomerization processes occur at some stage of the entire process. The theoretical analysis and the fragmentation pattern of the spectrum has allowed the assignment of the most likely structure to the radical observed.

On the doublet [B, C, N, O, F] PES, six structures have been located (Figure 3): **1** and **1a** of FBNCO connectivity, **2** and **2a** of FBOCN connectivity, the ring structure **3** and the branched-chain structure **4** where the boron atom is three-coordinate. Saddle points have been identified connecting **1** to **1a**, the ring structure **3** to both **1a** and **2**, and **2** to both **2a** and **4** (Figure 4). The linear structures of the ions do not match those of the radicals, which are therefore predicted to be formed with some excess of energy by the vertical process. In particular, the vertical neutralization energy of the open-chain FBOCN radicals, **2** and **2a**, from **2**$^+$ is computed to amount to 70.8 and 69.3 kcal mol$^{-1}$, respectively. Such an excess of energy is well above the lowest dissociation energy into FBO and CN, which rules out the survival and detection of the FBOCN radical.

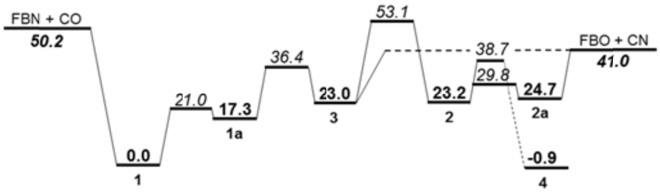
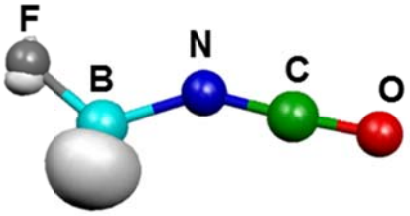


Figure 4. Schematic energy diagram of the [B, C, N, O, F] potential energy surface. Enthalpy values (kcal mol$^{-1}$) computed at CCSD(T)/aug-cc-pVTZ level of theory.

In contrast, the radicals of FBNCO connectivity, **1** and **1a**, are formed with 47.5 and 29.8 kcal mol$^{-1}$, respectively, that is below the lowest dissociation energy into FBN and CO. Nonetheless, this excess of energy would allow the dissociation into FBO and CN by an isomerization-dissociation process likely occurring in the microsecond time scale along the reaction path. Accordingly, the neutral fraction that does not survive dissociates into both FBN (+ CO) and FBO (+ CN); the presence of peaks at m/z 46 ($FBO^+$) and 26 ($CN^+$), more intense in the NR spectrum than in the CAD spectrum, is in good agreement with this scenario.

The experimental and theoretical evidence points to the detection of the FBNCO radical **1**, as the most likely candidate to survive the neutralization and isomerization-dissociation processes.



**Scheme 1**. Spin density plot of FBNCO **1** (B3LYP/aug-cc-pVTZ).

FBNCO **1** is a two-coordinate boron radical, with the unpaired electron mainly located on the boron atom (0.922 e$^-$) and the π overlap on the planar NCO group that significantly contributes to its stability (Scheme 1). FBNCO **1a** has instead the spin mainly located on the carbon atom (0.708 e$^-$) and partially on the oxygen (0.143 e$^-$) and boron (0.124 e$^-$) atoms. **1a** is less stable than **1** and, in addition, it is viable to isomerization to the ring structure **3**, due to the possible rotation of the N-C bond and the partial spin density on the oxygen atom. The most stable FBNCO isomer **1** is reasonably assigned to the detected neutral species, under the employed experimental conditions.

## Conclusions

We have reported the first experimental detection in the gas phase of the intriguing 35-electron species FBNCO. It has been prepared by vertical electron transfer to the $FBNCO^+$ ion, and has been observed for the minimum time of 0.8 microseconds. The theoretical analysis of the doublet [B, C, N, O, F] surface shows that FBNCO is a stable species with a dissociation energy of 50 kcal mol$^{-1}$ and an isomerization energy of 21 kcal mol$^{-1}$.

## Notes and references

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The experiments were performed using a TSQ700 mass spectrometer from Finnigan Ltd. and a modified ZABSpec oa-TOF instrument (VG Micromass) described elsewhere. [13] The elemental composition of the ions was unambiguously confirmed by CAD spectra of mass- and energy-selected precursor ions. The neutralization-reionization (NR) experiments, using Xe and $O_2$ as colliders, were performed as described elsewhere. [13] Experimental and computational details are described in the Supporting Information.

1 A. A. Korkin, A. Balkova, R. J. Bartlett, R. J. Boyd and P. v. R. Schleyer, *J. Phys. Chem.*, 1996, **100**, 5702.

2 F. Cacace, G. de Petris and A. Troiani, *Science*, 2002, **295**, 480.

3 M. Zhou, N. Tsumori, Q. Xu, G. P. Kushto and L. Andrews, *J. Am. Chem. Soc.*, 2003, **125**, 11371.

4 G. de Petris, F. Cacace, R. Cipollini, A. Cartoni, M. Rosi and A. Troiani, *Angew. Chem. Int. Ed.*, 2005, **44**, 462; R. A. Moss, G. S. Chu and R. R. Sauers *J. Am. Chem. Soc.*, 2005, **127**, 2408; C. J. Shaffer, B. J. Esselman, R. J. McMahon, J. F. Stanton and R. C. Woods, *J. Org. Chem.*, 2010, **75**, 1815; X. Zeng, H. Beckers, H. Willner and J. F. Stanton, *Angew. Chem. Int. Ed.*, 2011, **50**, 1720; A. Perrin, X. Zeng, H. Beckers and H. Willner *J. Mol. Spectr.*, 2011, **269**, 30; X. Zeng, H. Beckers, H. Willner and J. F. Stanton, *Eur. J. Inorg. Chem.*, 2012, **21**, 3403.

5 R. Hoffmann, P. v. R. Schleyer and H. F. Schaefer III, *Angew. Chem. Int. Ed. Engl.*, 2008, **47**, 7164.

6 G. R. Whittel and I. Manners, *Angew. Chem. Int. Ed.*, 2011, **50**, 10288; L. Song, Z. Liu, A. L. M. Reddy, N. T. Narayanan, J. Taha-Tijerina, J. Peng, G. Gao, J. Lou, R. Vajtai and P. M. Ajayan, *Adv. Mater.*, 2012, **24**, 4878.

7 M. Zhou, N. Tsumori, Z. H. Li, K. N. Fan, L. Andrews and Q. Xu, *J. Am. Chem. Soc.*, 2002, **124**, 12936; M. Zhou, Z. X. Wang, P. v. R. Schleyer and Q. Xu, *ChemPhysChem*, 2003, **4**, 763.

8 I. Cernusak, M. Urban, P. Ertl and R. J. Bartlett, *J. Am. Chem. Soc.*, 1992, **114**, 10955.

9 D. V. Lanzisera, L. Andrews and P. R. Taylor, *J. Phys. Chem.*, 1997, **101**, 7134.

10 D. J. Belson, A. N. Strachan, *Chem. Soc. Rev.*, 1982, **11**, 41.

11 F. Pepi, A. Ricci and M. Rosi, *J. Phys. Chem. B*, 2006, **110**, 4492; F. Pepi, A. Ricci, S. Garzoli and M. Rosi, *J. Phys. Chem. A*, 2006, **110**, 12427.

12 The potential energy surfaces of $FBNCO^+$ and FBNCO were investigated by locating the lowest stationary points at the B3LYP level of theory in conjunction with the correlation consistent valence polarized set aug-cc-pVTZ. The assignment of the saddle points was performed using intrinsic reaction coordinate (IRC) calculations. The energy of all the stationary points was computed at the higher level of calculation CCSD(T) using the same basis set aug-cc-pVTZ. See Supporting Information. A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623; T. H. Dunning Jr. *J. Chem. Phys.*, 1989, **90**, 1007; D. E. Woon and T. H. Dunning Jr. *J. Chem. Phys.*, 1993, **98**, 1358; R. A. Kendall, T. H. Dunning Jr. and R. J. Harrison, *J. Chem. Phys.*, 1992, **96**, 6796; C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.*, 1989, **90**, 2154; C. Gonzales and H. B. Schlegel, *J. Phys. Chem.*, 1990, **94**, 5523; R. J. Bartlett, *Annu. Rev. Phys. Chem.*, 1981, **32**, 359; K. Raghavachari, G. W. Trucks, J. A. Pople and M. Head-Gordon, *Chem. Phys Lett.*, 1989, **157**, 479; J. Olsen, P. Jorgensen, H. Koch, A. Balkova and R. J. Bartlett, *J. Chem. Phys.*, 1996, **104**, 8007; Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT (2009); *MOLEKEL 4.3*, P. Flükiger, H. P. Lüthi, S. Portmann and J. Weber, Swiss Center for Scientific Computing, Manno (Switzerland), 2000-2002; S. Portmann and H. P. Lüthi, *Chimia*, 2000, **54**, 766.

13 F. Bernardi, F. Cacace, G. de Petris, F. Pepi, I. Rossi and A. Troiani, *Chem. Eur. J.*, 2000, **6**, 537; G. de Petris, M. Rosi and A. Troiani, *J. Phys. Chem. A*, 2007, **111**, 6526.

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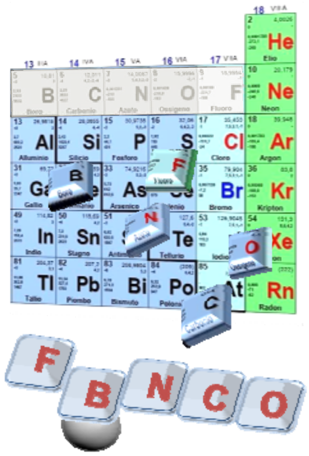

The new radical FBNCO and the new $FBNCO^+$ cation, containing all the p-block elements, have been identified in the gas phase, as species having a dissociation energy of 50 and 161 kcal $mol^{-1}$, respectively.