

Electronic Supporting Information for

A Valence Bond view of isocyanides electronic structure.

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VB Procedure

In VB theory, the wave function, Ψ is expressed as a linear combination of VB structures Φ_K :

$$\Psi = \sum_K C_K \Phi_K \quad (1)$$

The VB structures Φ_K correspond to all the possibilities of distributing the “active electrons” that participate in the interchanging bonds (here the π bonds) and the coefficient C_K correspond to the structure Φ_K .

Two subsets are used to build the VB wave function. The active orbitals are the only ones treated at the VB level (here the π orbitals) contrary to the remaining ones called “spectator orbitals”. As each of the nitrogen and the carbon atoms of the –NC bond bring two p orbitals, four active orbitals are defined during the calculation. The four active (VB) orbitals are held strictly localized on their specific centers, and their occupancy is determined by the considered VB structures, whereas the spectator orbitals take the form of doubly occupied (fixed occupancy) delocalized molecular orbitals.

In the VBSCF procedure, all the orbitals, spectator and active, as well as structural coefficients C_K are optimized simultaneously to minimize the total energy. As such, the VBSCF method takes care of the static electron correlation. However, to obtain quantitative accuracy it is necessary to take into account the dynamic correlation. As an improvement of VBSCF, the BOVB method allows the orbitals to be different in each VB structures, and as all structures are optimized in the presence of the others, the best compromise between optimal orbital set for a specific structure and maximization of the resonance between them is reached during the optimization process. As such, the BOVB method accounts for part of the dynamic correlation, while leaving the wave function as compact as at the VBSCF level. BOVB method can be used at different levels of calculation. The precise procedure used in the study is the following. First, a BOVB calculation in which all spectator orbitals are fully localized between one (lone pair) or two (bond) atoms is performed. Then in a second step, starting from this wave function, the active orbitals are held frozen while the inactive orbitals are allowed to delocalize over the whole

molecule. This two-step procedure helps to avoid convergence problems which may happen in particular in low-symmetry molecules, and has been referred to as the D-BOVB* level in the literature.¹

The weights of the VB structures are defined by the Coulson-Chirgwin formula,² which is the equivalent of a Mulliken population analysis (see Eq. (2)).

$$W_K = C_K^2 + \sum_{L \neq K} C_K C_L \langle \Phi_K | \Phi_L \rangle \quad (2)$$

VB structures definition

The VB system consisted in four electrons distributed in the four localized p orbitals of nitrogen and the terminal carbon atoms. A π bond is created by singlet-coupling two electrons respectively located one on a π orbital of the carbon atom, and the other on the corresponding π orbital of the nitrogen, whereas a lone pair is obtained when the two electrons of the pair are both located on the same atom. In the case of isocyanides, only the neutral and mono-ionic structures were selected among all the possible VB structures obtained by distributing two electrons in each π system. This leads to the six main VB structures depicted in Figure SI-1. These six VB structures lead to four different mesomeric forms when equivalent structures are grouped together, as two different VB structures can be defined for each of the forms **I** and **III**. By convention the C-N-C fragment is oriented along the z axis, and the two π systems along the x and y axis. In the case of the mesomeric form **I**, a first VB structure, noted **I_x**, considers a double bond along the x axis and the lone pair of the nitrogen along the y axis, while an equivalent second structure **I_y** can be obtained when the double bond is along y and the lone pair along x. For the sake of clarity, the weights indicated in the article are the sum of the weights of **I_x** and **I_y**. In the same way, the mesomeric form **III** leads to two equivalent VB structures according as the lone pair of the nitrogen is directed along the x or the y-axis while the carbon π lone pair is along the other one.

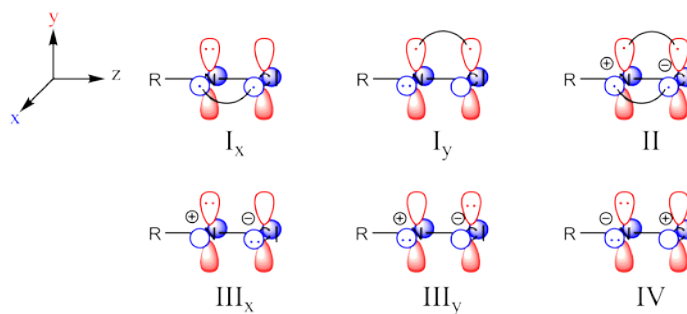


Figure SI-1. The six mesomeric forms used to describe isocyanides. The π -system is described in red and blue, and the σ one in black.

Computational details

All XMVB calculations have used the standard 6-31G(d) basis set, which is a basis set of double-zeta quality with polarization functions on atoms different from hydrogen. Diffuse orbitals may be added, such as in the 6-31+G(d) basis set. However, as shown in Table SI-2, results do not change upon addition of diffuse functions for the MeNC case, so for all molecules we stuck to the 6-31G(d) basis.

To take care of solvation effects, geometries were obtained with the Polarized Continuum Model with, in addition, a limited number of explicit solvent molecules. In the case of water, a first molecule was added close to the isocyanide carbon atom to interact with the σ lone pair. We added a second water molecule either close to the carbon atom or to the nitrogen atom. In both cases, the second water molecule moved to make a hydrogen bond with the first one leading to a stabilization of less than 1 kcal.mol⁻¹. We thus decided to use only one solvent molecule.

Me-NC	I	II	III	IV
6-31G(d)	51.2	28.6	8.9	11.3
6-31+G(d)	49.9	29.8	9.6	10.7

Table SI-1. Effect of the basis set on the mesomeric forms weights calculatated at the D-BOVB level.

Optimized geometries

BnNC

Energy: -362.77615725

N	-0.113074	0.255816	-0.054113
C	-0.230115	0.570196	1.083704
C	0.069050	-0.142937	-1.413413
C	1.312204	0.474146	-2.020180
C	2.486834	0.612872	-1.268633
C	3.642209	1.128806	-1.864794
C	3.635714	1.494316	-3.216579
C	2.463516	1.356366	-3.968430
C	1.305716	0.844298	-3.371582
H	0.132224	-1.236560	-1.430420
H	-0.818850	0.155230	-1.978470
H	0.392926	0.745104	-3.955664
H	2.448173	1.647950	-5.015055
H	4.533836	1.896966	-3.676604
H	4.547444	1.241823	-1.274472
H	2.492161	0.338498	-0.216789

CF₃NC

Energy: -429.61130175

C	0.000000	0.000000	-0.286462
F	0.000000	1.248088	-0.738877
F	1.080876	-0.624044	-0.738877
F	-1.080875	-0.624044	-0.738877
N	0.000000	0.000000	1.121471
C	0.000000	0.000000	2.309374

EtNC

Energy: -171.56588699

C	-0.176183	-0.371743	-1.441454
N	-0.092697	-0.121374	-0.285831
C	0.032817	0.215743	1.098730
C	0.880725	1.471843	1.276749
H	-0.974237	0.359943	1.497988
H	0.482876	-0.639372	1.609204
H	0.421807	2.316627	0.759322
H	1.882115	1.315005	0.871019
H	0.963185	1.710655	2.340121

MeNC

Energy: -132.36731579

C	0.000000	0.000000	-1.116138
H	-0.000003	1.029306	-1.476553
H	0.891406	-0.514650	-1.476553
H	-0.891403	-0.514656	-1.476553
N	0.000000	0.000000	0.309786
C	0.000000	0.000000	1.493803

iPrNC

Energy: -210.76692043

H	-0.049708	-0.107779	-1.516922
C	0.034091	0.113184	-0.447527
H	-2.052532	0.679019	-0.259806
N	0.490872	1.469557	-0.346687
C	0.868064	2.588843	-0.232991
H	-1.709664	-1.028370	0.102619
C	-1.340491	-0.004453	0.208061
H	-1.268604	0.237636	1.271913
C	1.068808	-0.814243	0.186607
H	1.175177	-0.583218	1.250030
H	2.041391	-0.697514	-0.296607
H	0.742595	-1.852662	0.081308

MeSO₂CH₂NC

Energy: -719.31981051

C	0.054590	-0.042568	0.013526
N	0.016351	-0.021016	1.200104
C	0.050487	0.003673	2.609863
H	-0.051102	-1.003714	3.019245
H	-0.732707	0.654625	3.007337
S	1.611401	0.713731	3.232304
O	1.586943	0.464133	4.667408
O	1.737543	2.055426	2.687894
C	2.847598	-0.321951	2.478572
H	3.803608	0.039499	2.862210
H	2.805930	-0.207230	1.395617
H	2.684951	-1.355412	2.787279

tBuNC

Energy: -249.96964916

C	0.000038	0.000038	-0.012525
N	-0.000062	0.000166	1.175113
C	-0.000371	0.000059	2.613868
C	1.456023	-0.000168	3.084693
C	-0.728534	1.261493	3.084302
C	-0.728875	-1.261249	3.084111
H	-0.743663	-1.286287	4.177975
H	-1.758342	-1.267101	2.715768
H	-0.219161	-2.155893	2.716250
H	1.484666	-0.000349	4.178563
H	1.975953	-0.888837	2.716646
H	1.976131	0.888519	2.716938
H	-0.743198	1.286435	4.178168
H	-0.218657	2.156050	2.716461
H	-1.758044	1.267621	2.716072

