

Valence Bond Structures for the N_3^- Anion, the $\text{N}_3\cdot$ Radical and the $\text{N}_6^{\cdot-}$ Radical Anion

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With Heitler-London atomic orbital-type formulations of the wave functions for (fractional) electron-pair $\pi_x(\text{NN})$ and $\pi_y(\text{NN})$ bonds, increased-valence structures for the N_3^- anion and $\text{N}_3\cdot$ radical are equivalent to resonance between familiar standard Lewis structures and singlet diradical (or “long-bond”) Lewis structures. Theory is developed for the calculation of the polarity parameters that are associated with the one-electron $\pi_x(\text{NN})$ and $\pi_y(\text{NN})$ bonds in the increased-valence structures, and illustrative STO-6G estimates of their values are reported. They show that the π_x and π_y electrons of these bonds are strongly charge-correlated relative to each other.

The increased-valence structures for the N_3^- anion and the $\text{N}_3\cdot$ radical are used to help construct increased-valence structures for the $\text{N}_6^{\cdot-}$ radical anion with C_{2h} symmetry.

Key words: Lewis Structures, Valence Bond (VB), Increased-valence, N_3^- Anion, $\text{N}_3\cdot$ Radical, $\text{N}_6^{\cdot-}$ Radical Anion

Introduction

Polynitrogen compounds are of general interest not only as high-energy density materials (HEDM) for propulsion and explosive applications [1], but also from the standpoint of quantum chemical calculations. Whereas neutral poly-nitrogen molecules have been calculated extensively [2–12], only recently cationic poly-nitrogen species such as the N_5^+ cation have become available [13, 14], and studied computationally [15, 16]. In the area of poly-nitrogen anions, apart from the well-known N_3^- anion [17], until recently, only the cyclic N_5^- anion has been reported experimentally and computationally [18]. The $\text{N}_6^{\cdot-}$ radical anion has now been identified spectroscopically in rare gas matrices by Raman spectroscopy [19]. It can be regarded as the product formed by the reaction between an N_3^- anion [20] and a neutral $\text{N}_3\cdot$ radical [21]. In this study, we focus attention on valence bond (VB) aspects of the electronic structures of the N_3^- anion, the $\text{N}_3\cdot$ radical and the $\text{N}_6^{\cdot-}$ radical anion.

The ground-state of the $\text{N}_6^{\cdot-}$ radical anion has been calculated [21] to have C_{2h} symmetry, with eight out-

of-plane π electrons, and b_u symmetry for the odd (in-plane) π electron orbital to give an electronic state of B_u symmetry. Here, initially we give consideration to VB structures of the Lewis and increased-valence types for the N_3^- anion and $\text{N}_3\cdot$ radical, and provide the results of STO-6G VB calculations for resonance between the Lewis structures that are components of the increased-valence structures. We shall then use the increased-valence structures for the N_3^- anion and $\text{N}_3\cdot$ radical to construct increased-valence structures for the $\text{N}_6^{\cdot-}$ radical anion, and show that the bond properties that are implied by resonance between these structures are in qualitative accord with the calculated bond lengths.

Valence Bond Structures and Calculations for the N_3^- Anion and $\text{N}_3\cdot$ Radical

For the linear N_3^- anion, resonance between the standard octet VB structures **1–4** of Fig. 1 provides the familiar Lewis-type VB representation of its electronic structure [22]. These structures can be stabilized *via* one-electron delocalisations of p_x and p_y

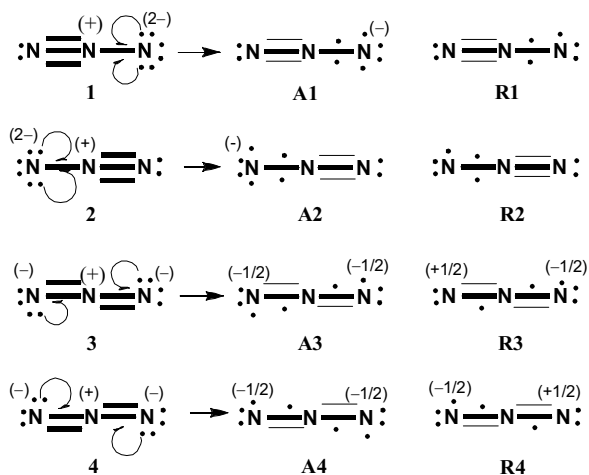


Fig. 1. Lewis structures **1–4** and increased-valence structures **A1–A4** for the N_3^- anion, and **R1–R4** for the N_3^\cdot radical. For illustrative purposes, atomic formal charges are assigned on the assumption [24] that bonding electrons are shared equally between pairs of adjacent atoms. The optimum values for the formal charges of course need to be determined variationally.

electrons from the terminal N^{2-} of structures **1** and **2** and the terminal N^- of structures **3** and **4** into bonding $\pi_x(NN)$ and $\pi_y(NN)$ molecular orbitals (MOs), as shown in Fig. 1. The delocalizations generate [23–26] the increased-valence structures **A1–A4** of Fig. 1, with one-electron $\pi_x(NN)$ and $\pi_y(NN)$ bonds and fractional electron-pair $\pi_x(NN)$ and $\pi_y(NN)$ bonds. (Thin bond lines are used to represent fractional electron-pair bonds [23–26].) Resonance between these four increased-valence structures is equivalent [26] to resonance between the canonical Lewis structures **1–9** of Fig. 2, when the wave functions for the normal $\pi_x(NN)$ and $\pi_y(NN)$ electron-pair bonds of **1–9** and the fractional $\pi_x(NN)$ and $\pi_y(NN)$ electron-pair bonds of **A1–A4** are formulated using Heitler-London (HL) atomic orbital (AO) procedures. If 2-center Coulson-Fischer-type [27] bonding MOs replace the AOs for the fractional electron-pair bonds, (for example, when $\phi'_{ab} = a + k'b$ and $\phi''_{ba} = b + k'a$ replace the AOs *a* and *b*), resonance between **A1–A4** is equivalent to resonance between the canonical Lewis structures **1–9** and 27 additional canonical Lewis structures [26].

In ref. [26], the results of semi-empirical ($S = 0$ spin) VB calculations are reported for the N_3^- anion. These calculations include the wave functions for the 36 canonical Lewis structures, and show that singlet

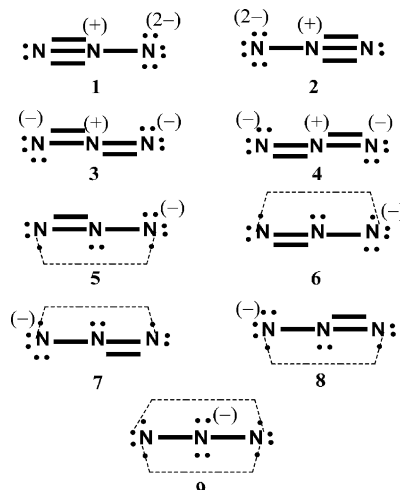


Fig. 2. Component Lewis structures **1–9** for the N_3^- anion increased-valence structures **A1–A4**.

diradical/Dewar/“long-bond” structures, such as **5–9** of Fig. 2, have substantial weights.

In Table 1, we report the results of STO-6G VB calculations for resonance between the N_3^- anion structures **1–9** of Fig. 2, with the same set of AOs in each structure. The calculations were performed using the Roso [28–31] program (see Appendix A). These results show also that the singlet diradical structures **5–8** are important Lewis-type VB structures.

The results of *ab initio* VB studies with better basis sets for numerous other 1,3-dipolar (or “zwitterionic biradical hybrid”) [32, 33] molecules and ions also show that singlet diradical structures are important Lewis structures for their ground-state resonance schemes [34–37].

The VB calculations can of course be elaborated by using a number of procedures, for example (but not only) with different $2p_x$ and $2p_y$ AOs in each of the Lewis structures, and by replacing (i) $(2p)^2$ by $(2p')^1(2p'')^1$ and (ii) increased-valence configurations of the type $(a)^1(a + kb)^1(b)^1(c)^1$ with $(a)^1(a +$

Table 1. The N_3^- anion. Coefficients C_i and structural weights for canonical structure wave functions ψ_i in $\Psi = \sum C_i \psi_i$.

Lewis VB structure	C_i un-normalized	Structural weight
1, 2	0.089204	0.04962
3, 4	0.199621	0.15631
5, 6, 7, 8	–0.176982	0.12750
9	0.116218	0.07811

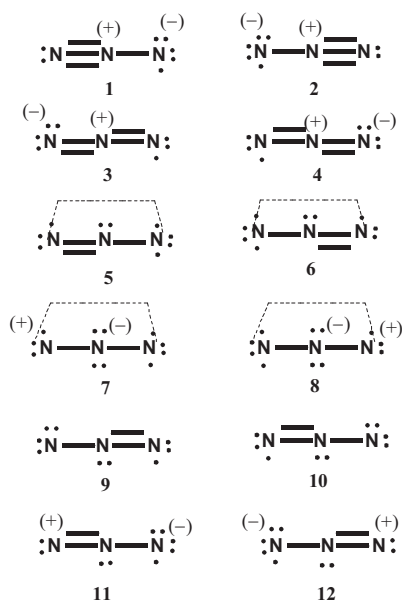


Fig. 3. Component $N_3\cdot$ radical Lewis structures **1–12** for resonance between the increased-valence structures **R1–R4**.

$kb')^1(b)^1(c)^1$ with $b' \neq b$ (cf. ref. [38] for example). However here, these elaborations are not needed in order to show that the $\pi_x(NN)$ and $\pi_y(NN)$ electrons of the one-electron bonds of increased-valence structures are substantially electron-charge correlated.

When a p_x electron is removed from a terminal nitrogen atom of the increased-valence structures **A1–A4** for the N_3^- anion, the increased-valence structures **R1–R4** of Fig. 1 are obtained for the $N_3\cdot$ radical. Resonance between increased-valence structures **R1–R4** is equivalent to resonance between the Lewis structures **1–12** of Fig. 3. In Table 2, we report the results of VB calculations similar to those of Table 1 for resonance

Table 2. The $N_3\cdot$ radical. Coefficients C_i and structural weights for canonical structure wave functions ψ_i in $\Psi = \sum C_i \psi_i$.^a

Lewis VB structure	C_i un-normalized	Structural weight
1, 2	0.113054	0.08825
3, 4	-0.125162	0.10316
5, 6	-0.159536	0.14261
7, 8	-0.095690	0.03389
9, 10	0.229347	0.10230
11, 12	0.097025	0.02980

^a In the Supporting Information, the un-normalized C_i coefficients are reported for **A1**, **A1** \leftrightarrow **A2**, **A3**, **A3** \leftrightarrow **A4**, **R1**, **R1** \leftrightarrow **R2**, **R3** and **R3** \leftrightarrow **R4**.

between these twelve Lewis structures. The doublet diradical structures **5** and **6** with zero atomic formal charges, as well as structures **9** and **10**, also with zero atomic formal charges, are calculated to be important structures.

Bond Polarity Parameters for N_3^- and $N_3\cdot$ Increased-valence Structures: Theory

Orbitals for the increased-valence structures

For the increased-valence structures **A1–A4** for the N_3^- anion and **R1–R4** for the $N_3\cdot$ radical, the electrons that form two one-electron bonds (one π_x and one π_y) occupy two of the bonding MOs of either Eq. 1 or 2.

$$\begin{aligned} \varphi(k)_{ab} &= a + kb, & \varphi(k)_{cb} &= c + kb, \\ \varphi(l)_{de} &= d + le, & \varphi(l)_{fe} &= f + le \end{aligned} \quad (1)$$

$$\begin{aligned} \varphi(l)_{ab} &= a + lb, & \varphi(l)_{cb} &= c + lb, \\ \varphi(k)_{de} &= d + ke, & \varphi(k)_{fe} &= f + ke \end{aligned} \quad (2)$$

In these equations, a, b and c are the p_x AOs, d, e and f are the p_y AOs, and $k = k_1 = k_2$ and $l = l_1 = l_2$ are bond polarity parameters (see also Fig. 4).

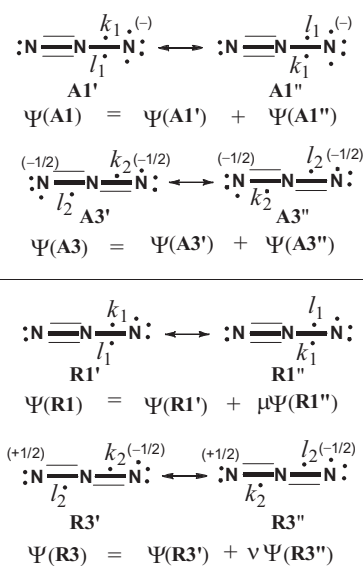


Fig. 4. Assignment of k and l polarity parameters to the increased-valence structures. For the $N_3\cdot$ radical, there are uneven numbers of π_x and π_y electrons. Therefore it is necessary to write $\Psi(\mathbf{R1}) = \Psi(\mathbf{R1}') + \mu\Psi(\mathbf{R1}'')$, $\Psi(\mathbf{R2}) = \Psi(\mathbf{R2}') + \mu\Psi(\mathbf{R2}'')$, $\Psi(\mathbf{R3}) = \Psi(\mathbf{R3}') + \nu\Psi(\mathbf{R3}'')$, $\Psi(\mathbf{R4}) = \Psi(\mathbf{R4}') + \nu\Psi(\mathbf{R4}'')$. For each of the resonance schemes, use of $k_1 = k_2 = k$ and $l_1 = l_2 = l$ gives the energy minimum.

Wave functions and polarity parameters for the N_3^- anion

With the p_x and p_y AOs and MOs of Eqs. 1 and 2, the two equivalent $S = 0$ spin wave functions of Eqs. 3 and 4 can be constructed for increased-valence structure **A1** of Fig. 2.

$$\begin{aligned} \Psi(\mathbf{A1}') = & |a^\alpha \varphi_{ab}^\beta b^\alpha c^\beta d^\alpha \varphi_{de}^\beta e^\alpha f^\beta| \\ & + |\varphi_{ab}^\alpha a^\beta c^\alpha b^\beta d^\alpha \varphi_{de}^\beta e^\alpha f^\beta| \\ & + |a^\alpha \varphi_{ab}^\beta b^\alpha c^\beta \varphi_{de}^\alpha d^\beta f^\alpha e^\beta| \\ & + |\varphi_{ab}^\alpha a^\beta c^\alpha b^\beta \varphi_{de}^\alpha d^\beta f^\alpha e^\beta| \quad (3) \\ \propto & |\varphi_{ab}^\alpha \varphi_{ab}^\beta \varphi_{ab}^* c^\beta \varphi_{de}^\alpha \varphi_{de}^\beta \varphi_{de}^* e^\alpha f^\beta| \\ & + |\varphi_{ab}^\alpha \varphi_{ab}^\beta c^\alpha \varphi_{ab}^* \varphi_{de}^\alpha \varphi_{de}^\beta \varphi_{de}^* e^\alpha f^\beta| \\ & + |\varphi_{ab}^\alpha \varphi_{ab}^\beta \varphi_{ab}^* c^\beta \varphi_{de}^\alpha \varphi_{de}^\beta f^\alpha \varphi_{de}^* e^\beta| \\ & + |\varphi_{ab}^\alpha \varphi_{ab}^\beta c^\alpha \varphi_{ab}^* \varphi_{de}^\alpha \varphi_{de}^\beta f^\alpha \varphi_{de}^* e^\beta| \quad (4) \end{aligned}$$

with $\varphi_{ab} = a + kb$ and $\varphi_{de} = d + le$.

$$\begin{aligned} \Psi(\mathbf{A1}'') = & |a^\alpha \varphi_{ab}^\beta b^\alpha c^\beta d^\alpha \varphi_{de}^\beta e^\alpha f^\beta| \\ & + |\varphi_{ab}^\alpha a^\beta c^\alpha b^\beta d^\alpha \varphi_{de}^\beta e^\alpha f^\beta| \\ & + |a^\alpha \varphi_{ab}^\beta b^\alpha c^\beta \varphi_{de}^\alpha d^\beta f^\alpha e^\beta| \\ & + |\varphi_{ab}^\alpha a^\beta c^\alpha b^\beta \varphi_{de}^\alpha d^\beta f^\alpha e^\beta| \quad (5) \end{aligned}$$

with $\varphi_{ab} = a + lb$ and $\varphi_{de} = d + ke$.

In Eq. 4, with four singly-occupied orbitals, the φ^* orbitals are antibonding MOs that are orthogonal to the bonding φ MOs constructed from the same AOs. Eq. 3 is obtained from Eq. 4 *via* unitary transformations of pairs of φ and φ^* MOs with the same electron spin. Similar types of identities occur for each of the $S = 0$ or $S = 1/2$ spin wave functions for all of the increased-valence structures for the N_3^- anion and $N_3\cdot$ radical. In each of Eqs. 3 and 5, a-b, d-e, φ_{cb} -c and φ_{fe} -f (fractional) electron-spin pairings occur.

Each increased-valence structure in Fig. 1 is equivalent to resonance between four of the Lewis structures in Figs. 2 and 3. The polarity parameters are determined by expressing the $S = 0$ or $S = 1/2$ spin wave functions for the increased-valence structures as linear combinations of the $S = 0$ or $S = 1/2$ spin wave functions for their component Lewis structures, and then equating the coefficients of these linear combinations with the calculated (un-normalized) C_i coefficients for resonance between the relevant Lewis structures. For

example, for $\Psi(\mathbf{A1}) = \Psi(\mathbf{A1}') + \Psi(\mathbf{A1}'')$ we have

$$\Psi(\mathbf{A1}') = \psi_1 - l_1 \psi_5 - k_1 \psi_6 + k_1 l_1 \psi_9 \quad (6)$$

$$\Psi(\mathbf{A1}'') = \psi_1 - k_1 \psi_5 - l_1 \psi_6 + k_1 l_1 \psi_9 \quad (7)$$

to give

$$\begin{aligned} \Psi(\mathbf{A1}) = & \Psi(\mathbf{A1}') + \Psi(\mathbf{A1}'') \\ = & 2\psi_1 - (k_1 + l_1)(\psi_5 + \psi_6) + 2k_1 l_1 \psi_9 \quad (8) \end{aligned}$$

$$\equiv C_1 \psi_1 + C_5 (\psi_5 + \psi_6) + C_9 \psi_9 \quad (9)$$

and

$$C_5/C_1 = -1/2(k_1 + l_1) \text{ and } C_9/C_1 = k_1 l_1. \quad (10)$$

When all of the increased-valence structures participate in resonance, *i. e.* $(\mathbf{A1}') \leftrightarrow (\mathbf{A1}'') \leftrightarrow (\mathbf{A2}') \leftrightarrow (\mathbf{A2}'') \leftrightarrow (\mathbf{A3}') \leftrightarrow (\mathbf{A3}'') \leftrightarrow (\mathbf{A4}') \leftrightarrow (\mathbf{A4}'')$, with $k_1 = k_2 = k$ and $l_1 = l_2 = l$ the wave functions for the increased-valence structures $(\mathbf{A2}')$, $(\mathbf{A2}'')$, $(\mathbf{A3}')$, $(\mathbf{A3}'')$, $(\mathbf{A4}')$ and $(\mathbf{A4}'')$ are given by Eqs. B.1–B.6 of Appendix B. The resulting wave functions for $\Psi(\mathbf{A1}) + \Psi(\mathbf{A2}) + \rho\{\Psi(\mathbf{A3}) + \Psi(\mathbf{A4})\}$ are then those of Eqs. 11 and 12

$$\begin{aligned} \Psi(N_3^{(-)}) = & \Psi(\mathbf{A1}) + \Psi(\mathbf{A2}) + \rho\{\Psi(\mathbf{A3}) + \Psi(\mathbf{A4})\} \\ = & 2(\psi_1 + \psi_2) + 2\rho(\psi_3 + \psi_4) - (k+l)(1+\rho) \\ & \cdot (\psi_5 + \psi_6 + \psi_7 + \psi_8) + 4(1+\rho)kl\psi_9 \quad (11) \end{aligned}$$

$$\equiv C_1(\psi_1 + \psi_2) + C_3(\psi_3 + \psi_4) + C_5(\psi_5 + \psi_6 + \psi_7 + \psi_8) + C_9\psi_9 \quad (12)$$

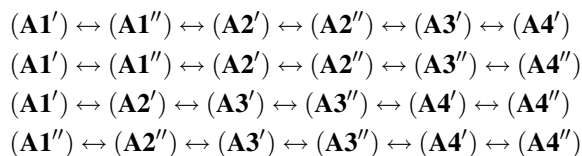
With $d_i = C_i/C_1$, equating coefficients in these equations gives

$$\begin{aligned} \rho = & d_3, \quad kl = d_9/\{2(1+\rho)\} \text{ and} \\ k+l = & -2d_5/(1+\rho) \quad (13) \end{aligned}$$

and hence Eq. 14 for the calculation of k and l

$$\begin{aligned} 2(1+d_3)k^2 + 4d_5k + d_9 = & 0 \text{ and} \\ l = & d_9/\{2(1+d_3)k\} \quad (14) \end{aligned}$$

It is noted that Eq. 14 can also be obtained *via* any of the following six structure resonance schemes.



Each of them involves three pairs of symmetrically-equivalent increased-valence structures.

Wave functions and polarity parameters for the $N_3\cdot$ radical

For increased-valence structure **R1**, the $S = M_S = +1/2$ spin wave functions are

$$\Psi(\mathbf{R1}') = |a^\alpha \varphi_{ab}^\beta b^\alpha c^\beta \varphi_{de}^\alpha e^\beta f^\alpha| + |\varphi_{ab}^\alpha a^\beta c^\alpha b^\beta \varphi_{de}^\alpha e^\beta f^\alpha| \\ + |a^\alpha \varphi_{ab}^\beta b^\alpha c^\beta \varphi_{de}^\alpha f^\beta e^\alpha| + |\varphi_{ab}^\alpha a^\beta c^\alpha b^\beta \varphi_{de}^\alpha f^\beta e^\alpha| \quad (15)$$

with $\varphi_{ab} = a + kb$ and $\varphi_{de} = d + le$ and

$$\Psi(\mathbf{R1}'') = |a^\alpha \varphi_{ab}^\beta b^\alpha c^\beta \varphi_{de}^\alpha e^\beta f^\alpha| \\ + |\varphi_{ab}^\alpha a^\beta c^\alpha b^\beta \varphi_{de}^\alpha e^\beta f^\alpha| + |a^\alpha \varphi_{ab}^\beta b^\alpha c^\beta \varphi_{de}^\alpha f^\beta e^\alpha| \\ + |\varphi_{ab}^\alpha a^\beta c^\alpha b^\beta \varphi_{de}^\alpha f^\beta e^\alpha| \quad (16)$$

with $\varphi_{ab} = a + lb$ and $\varphi_{de} = d + ke$.

$\Psi(\mathbf{R1}')$ and $\Psi(\mathbf{R1}'')$ are non-equivalent wave functions. Therefore it is necessary to write $\Psi(\mathbf{R1}) = \Psi(\mathbf{R1}') + \mu\Psi(\mathbf{R1}'')$, for which

$$\Psi(\mathbf{R1}') = \psi_1 - k\psi_5 - l\psi_{10} + kl\psi_8 \quad (17)$$

$$\Psi(\mathbf{R1}'') = \psi_1 - l\psi_5 - k\psi_{10} + kl\psi_8. \quad (18)$$

We then obtain

$$\Psi(\mathbf{R1}) = \Psi(\mathbf{R1}') + \mu\Psi(\mathbf{R1}'') \\ = (1 + \mu)\psi_1 - (k + \mu l)\psi_5 - (l + \mu k)\psi_{10} \\ + kl(1 + \mu)\psi_8 \quad (19) \\ \equiv C_1\psi_1 + C_5\psi_5 + C_{10}\psi_{10} + C_{12}\psi_8. \quad (20)$$

Using Eq. 19, together with the $\Psi(\mathbf{R2}') + \mu\Psi(\mathbf{R2}'')$, $\Psi(\mathbf{R3}') + \nu\Psi(\mathbf{R3}'')$ and $\Psi(\mathbf{R4}') + \nu\Psi(\mathbf{R4}'')$ obtained from Eqs. B.7–B.12 of Appendix B, the resulting equations for the $(\mathbf{R1}') \leftrightarrow (\mathbf{R1}'') \leftrightarrow (\mathbf{R2}') \leftrightarrow (\mathbf{R2}'') \leftrightarrow (\mathbf{R3}') \leftrightarrow (\mathbf{R3}'') \leftrightarrow (\mathbf{R4}') \leftrightarrow (\mathbf{R4}'')$ resonance are those of Eqs. 21–23:

$$\Psi(N_3\cdot) = \Psi(\mathbf{R1}') + \mu\Psi(\mathbf{R1}'') - \Psi(\mathbf{R2}') - \mu\Psi(\mathbf{R2}'') \\ + \rho \{ \Psi(\mathbf{R3}') + \nu\Psi(\mathbf{R3}'') - \Psi(\mathbf{R4}') - \nu\Psi(\mathbf{R4}'') \} \quad (21)$$

$$= (1 + \mu)(\psi_1 - \psi_2) - \rho(1 + \nu)(\psi_3 - \psi_4) \\ - \{k + \mu l + \rho(k + \nu l)\}(\psi_5 - \psi_6) \\ - kl\{1 + \mu + \rho(1 + \nu)\}(\psi_7 - \psi_8) \quad (22)$$

$$+ (l + \mu k)(\psi_9 - \psi_{10}) + \rho(l + \nu k)(\psi_{11} - \psi_{12}) \\ \equiv C_1(\psi_1 - \psi_2) + C_3(\psi_3 - \psi_4) + C_5(\psi_5 - \psi_6) \\ + C_7(\psi_7 - \psi_8) + C_9(\psi_9 - \psi_{10}) + C_{11}(\psi_{11} - \psi_{12}) \quad (23)$$

By equating coefficients in Eqs. 22 and 23, we obtain the kl , μ , ν and ρ equations of Eq. 24, in which $d_i = C_i/C_1$:

$$\rho(1 + \nu) = -d_3(1 + \mu), \\ \rho(k + \nu l) = -\{k + \mu l + d_5(1 + \mu)\}, \\ \rho(1 + \nu)kl = -(1 + \mu)(kl + d_7), \\ l + \mu k = (1 + \mu)d_9, \quad \rho(l + \nu k) = (1 + \mu)d_{11}. \quad (24)$$

By eliminating ρ , μ and ν we obtain Eq. 23 for k and l

$$(d_3 - 1)k^2 + (-d_5 + d_9 + d_{11})k + d_7 = 0; \\ l = d_7 / \{(1 - d_3)k\}. \quad (25)$$

For each set of increased-valence structures considered in Tables 3 and 4, the equations that relate the C_i coef-

Table 3. Energies (E) and k and l bond parameters for the standard Lewis structures **1–4** and increased-valence structures **A1–A4** of the N_3^- anion of Fig. 1. Sets of k and l values obtained from Eqs. 10, 14, 25 and those provided in the Supporting Information were checked by recalculating the energies using the wave functions for the relevant increased-valence structures.

Structure(s)	k	l	E (au)
A1	0.0	0.0	-161.81949
	3.8910	0.3583	-162.32978
A1 \leftrightarrow A2	0.0	0.0	-161.84599
	4.9056	0.1784	-162.47412
A3	0.0	0.0	-162.23498
	1.0865	0.3744	-162.43918
A3 \leftrightarrow A4	0.0	0.0	-162.25844
	1.7569	0.1750	-162.55142
A1 \leftrightarrow A2 \leftrightarrow A3 \leftrightarrow A4	0.0	0.0	-162.34704
	1.0302	0.1953	-162.58627

Table 4. Energies (E), and k and l bond parameters for the standard Lewis structures **1–4** of Fig. 3 of the $N_3\cdot$ radical and the increased-valence structures **R1–R4** of Fig. 1. $i = \sqrt{-1}$.

Structure(s)	k	l	E (au)
R1	0.0	0.0	-162.23581
	2.2866	0.1973	-162.50541
R1 \leftrightarrow R2	0.0	0.0	-161.30838
	1.8446	0.3158	-162.61797
R3	0.0	0.0	-162.23587
	1.5320	0.2443	-162.46895
R3 \leftrightarrow R4	0.0	0.0	-162.30844
	0.7356	0.7356	-162.57251
	+0.2022 <i>i</i>	-0.2022 <i>i</i>	-162.57251
	0.7629	0.7629	-162.55667
R1 \leftrightarrow R2 \leftrightarrow R3 \leftrightarrow R4	0.0	0.0	-162.39018
	1.8189	0.2208	-162.67826

ficients to the polarity parameters give the minimum energy.

Bond Polarity Parameters for N_3^- and N_3^\cdot Increased-valence Structures: STO-6G Estimates

The un-normalized C_i coefficients in Tables 1 and 2, and those reported in the Supporting Information, have been used to calculate the k and l MO bond parameters reported in Tables 3 and 4 for sets of increased-valence structures. Solution of each quadratic equation in k or l (namely Eqs. 10, 14, 19 and those of the Supporting Information) gives two values for these parameters, either k_+ and k_- or l_+ and l_- , with $k_+ = l_-$ and $k_- = l_+$. In Tables 3 and 4, values are reported for k_+ and l_- .

Energies are also reported in these Tables. The energy-optimized sigma electron cores for the **A1** \leftrightarrow **A2** \leftrightarrow **A3** \leftrightarrow **A4** and **R1** \leftrightarrow **R2** \leftrightarrow **R3** \leftrightarrow **R4** resonances have been used in each calculation.

For all but one of the calculations, the values of the k and l parameters differ substantially, showing that the $\pi_x(\text{NN})$ and $\pi_y(\text{NN})$ electrons are strongly charge-correlated relative to each other. However, when $k \neq l$, the k and l values are similar but complex for **R3** \leftrightarrow **R4**. For this resonance, a higher energy is also reported for $k = l$ (via $kl = C_7/C_3$, cf. Supporting Information), for which no charge correlation occurs between the $\pi_x(\text{NN})$ and $\pi_y(\text{NN})$ electrons.

Structures **A3** and **A4** are the lower energy structures for the N_3^- anion. With the (non-optimized) atomic formal charges displayed in Fig. 1, **A3** and **A4** involve better separation of these charges than do **A1** and **A2**. For the N_3^\cdot radical, structures **R1** and **R2**, with zero atomic formal charges (as displayed in Fig. 1), are more stable than are **R3** and **R4**. It must be noted however, that the energy of -162.58627 au for the **A1** \leftrightarrow **A2** \leftrightarrow **A3** \leftrightarrow **A4** resonance lies above the -162.67826 au for the **R1** \leftrightarrow **R2** \leftrightarrow **R3** \leftrightarrow **R4** resonance, *i. e.* the anion is calculated to be unbound. However a “consensus” [39] value of 2.71 eV has been derived [39] for the electron affinity of the N_3^\cdot radical.

N–N Bond Lengths

Empirical estimates [40] of “standard” single, double and triple N–N bond lengths are 1.449 (H_2NNH_2), 1.252 ($HNNH$) and 1.098 Å (N_2). For the N_3^- anion and the N_3^\cdot radical, the N–N bond lengths [41, 42] of 1.188 and 1.181 Å are intermediate between those for the “standard” N–N double and triple bonds. It is of

course recognized that the N–N σ bond hybridization for the two azide species differs from that of $HN=NH$, and this difference as well as the π bonding affects the lengths of the bonds. Be that as it may, inspection of the more-stable increased-valence structures **A1–A4** and **R1–R4** shows that these structures involve more N–N π bonding than do the Lewis structures **1–4** in each of Figs. 1, 2 and 3. Resonance between the Lewis structures **1–4** for either species implies that the N–N bonds are essentially double bonds.

With a , b and c as the p_x AOs, and d , e and f as the p_y AOs, the bonding MO configuration $(a + kb + c)^2(a - c)^2(d + ke + f)^2(d - f)^2$ is equivalent to a restricted form of resonance between the increased-valence structures **A1–A4** when one-parameter Coulson-Fischer bond orbitals are used to accommodate the electrons that form the fractional electron-pair π bonds in these structures (*cf.* the identity of ref. [43] for each set of 4-electron 3-center bonding units).

Valence Bond Structures for the $N_6^{\cdot-}$ Radical Anion

In ref. [21], the $N_6^{\cdot-}$ radical anion as the *trans* form $\{(N_1-N_2-N_3)-(N_4-N_5-N_6)\}^{(-)}$ was calculated to have a planar geometry, with the following bond length: $N_1-N_2 = N_5-N_6 = 1.16$ Å; $N_2-N_3 = N_4-N_5 = 1.20$ Å; $N_3-N_4 = 2.34$ Å. The bond angles were assigned the following values: $\angle N_1-N_2-N_3 = \angle N_4-N_5-N_6 = 180^\circ$, $\angle N_2-N_3-N_4 = \angle N_3-N_4-N_5 = 90^\circ$. The (non-symmetrical) azido bond lengths are similar to, but not identical with, those for the symmetrical N_3^- anion and N_3^\cdot radical. The calculated length of 2.34 Å for the intermolecular N_3-N_4 bond is substantially longer than the “standard” single bond length of 1.45 Å for H_2NNH_2 , which suggests that the stability of the $N_6^{\cdot-}$ radical anion relative to its triatomic azido components might not arise primarily from weak intermolecular σ bonding.

To generate increased-valence structures (designated as **AR**) for the $N_6^{\cdot-}$ radical anion, pairs of increased-valence structures for the N_3^- anion and the N_3^\cdot radical are juxto-positioned, as in Fig. 5. An electron is then delocalized from the N_3 atom of the N_3^- anion into an N_3-N_4 bonding MO, to give an intermolecular one-electron bond in each of the VB structures, as occurs in each of the **AR** increased-valence structures of Fig. 5. This bond could be either σ or

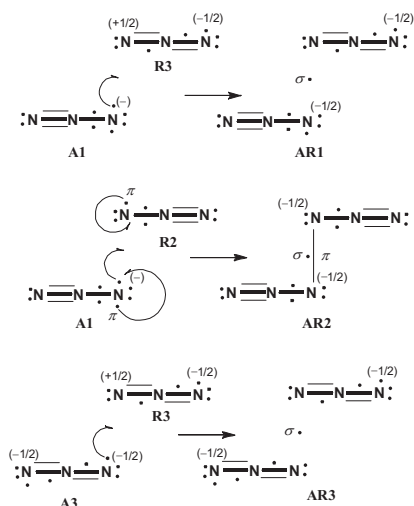


Fig. 5. Generation of increased-valence structures for the N_6^- radical anion from increased-valence structures **A1** and **A3** for the N_3^- anion and **R2** and **R3** for the N_3^\cdot radical. The mirror-image [center-inverted structure] for increased-valence structure **AR1** is not displayed. Because **AR2** involves four singly-occupied π electron orbitals, namely a' , $\varphi_{b'e'}$, $\varphi_{d'e'}$ and f' , for which $a'-f'$ are π electron AOs, two $S=0$ spin Rumer diagrams are associated with it to obtain N_1-N_2 , N_3-N_4 and N_5-N_6 π bonding.

π , but it is better energetically for it to be σ , so that the overall symmetry of the molecule is B_u rather than A_u . The results of the *ab initio* VB and MO calculations [21] show that this is the case.

As well as the one-electron N_3-N_4 σ bond, a fractional electron-pair N_3-N_4 π bond is present in the increased-valence structure **AR2**. Because the N_3-N_4 (Slater) π electron AO overlap integral is much smaller than the σ electron AO overlap integral ($\langle 2p\pi_3|2p\pi_4 \rangle = 0.015$, $\langle 2p\sigma_3|2p\sigma_4 \rangle = 0.082$, for an orbital exponent of 1.95), the fractional N_3-N_4 π bond will have negligible strength.

In accord with the calculated bond lengths for the N_6^- radical anion, resonance between the four **AR** increased-valence structures generates greater N–N bonding for the N_1-N_2 and N_5-N_6 pairs of atoms than it does for the N_2-N_3 and N_4-N_5 pairs of atoms. Because **AR3** of Fig. 5 separates better the formal negative charges, than do the other **AR** increased-valence structures, possibly it is the primary increased-valence structure.

Each of the N_6^- radical anion increased-valence structures of Fig. 5 involves a symmetrical 7-electron 6-center bonding unit of the type

$N_1-N_2 \cdot N_3 \cdot N_4 \cdot N_5-N_6$. (Non-displayed) $(N_3^\cdot)(N_3^-)$ and $(N_3^-)(N_3^\cdot)$ types of increased-valence structures can also be constructed. They involve non-symmetrical 7-electron 6-center bonding units such as $N_1-N_2 \cdot N_3 \cdot N_4-N_5 \cdot N_6$.

Conclusions

As has been done again here and previously [24] for the N_3^- anion, we have shown how increased-valence structures for the N_3^\cdot radical can be constructed using one-electron delocalizations from non-bonding AOs of Lewis VB structures into 2-center bonding MOs. We have also used a one-electron $N_3^- \rightarrow N_3^\cdot$ delocalization to form an intermolecular one-electron σ bond between each pair of N_3^- anion and N_3^\cdot radical increased-valence structures. Increased-valence structures of the type $(N_3 \cdot N_3)^-$ for the N_6^- radical anion are thereby generated. In accord with what has been calculated for this radical anion [21], the presence of the intermolecular one-electron N_3-N_4 bond in each of its increased-valence structures implies that the N_3-N_4 bond of the N_6^- radical anion should be substantially longer than an N–N single bond. Finally, as discussed in ref. [38] (and ref. [43] therein), it is noted that a one-electron delocalization from a doubly-occupied AO is preferred to a concerted two-electron delocalization from this AO.

Appendix A : Method for STO-6G calculations

The *ab initio* STO-6G VB calculations, with N–N bond lengths [41, 42] of 1.188 and 1.181 Å for the N_3^- anion and N_3^\cdot radical, resp., were performed using the program of Roso [28, 29]. The calculations used the nitrogen “best-atom” 1s exponent [44], and energy-optimized 2s and 2p exponents for each atom, for which we have assumed that $\zeta_{2s} = \zeta_{2p}$. The 14 σ electrons were accommodated in the **ABC** orbital configuration, $(1s_A)^2(1s_B)^2(1s_C)^2(l_A)^2(l_C)^2(\sigma_{AB})^2(\sigma_{CB})^2$, in which $l_A = 2s_A - v2p\sigma_A$, $l_C = 2s_C + v2p\sigma_C$, $\sigma_{AB} = 2p\sigma_A + v2s_A + \lambda(2s_B - 2p\sigma_B)$ and $\sigma_{CB} = -2p\sigma_C + v2s_C + \lambda(2s_B + 2p\sigma_B)$. For diatomic N_2 , the hybridization parameter v was determined variationally [45] to have a value of 0.35, and we have used this value in the N_3^- anion and the N_3^\cdot radical calculations. The energy-optimized values for λ and $\zeta_{2s} = \zeta_{2p}$ are:

N_3^- anion: $\lambda = 1.0$. Atoms **A** and **C**: $\zeta_{2s} = \zeta_{2p} = 1.86$; Atom **B**: $\zeta_{2s} = \zeta_{2p} = 2.01$.

N_3 radical: $\lambda = 1.0$. Atoms **A** and **C**: $\zeta_{2s} = \zeta_{2p} = 1.94$; Atom **B**: $\zeta_{2s} = \zeta_{2p} = 2.04$.

The structural weights in Tables 1 and 2 were calculated using the Chirgwin-Coulson formula [46].

Appendix B : Increased-valence structure wave functions in terms of Lewis structure wave functions

The N_3^- anion

When the increased-valence structures **A1**–**A4** participate in resonance, the resulting wave function is given by Eqs. 11 and 12, in which $\Psi(\mathbf{A1}) = \Psi(\mathbf{A1}') + \Psi(\mathbf{A1}'')$, $\Psi(\mathbf{A2}) = \Psi(\mathbf{A2}') + \Psi(\mathbf{A2}'')$, $\Psi(\mathbf{A3}) = \Psi(\mathbf{A3}') + \Psi(\mathbf{A3}'')$, and $\Psi(\mathbf{A4}) = \Psi(\mathbf{A4}') + \Psi(\mathbf{A4}'')$, [cf. Figure 4 for $\Psi(\mathbf{A1})$ and $\Psi(\mathbf{A3})$] In terms of the (non-normalized) ψ_i for the nine Lewis structures of Fig. 1, the $\Psi(\mathbf{Ai}')$ and $\Psi(\mathbf{Ai}'')$ are given by Eqs. 6 and 7 (with $k_1 = k$ and $l_1 = l$) for $\mathbf{i} = 1$ and Eqs. B.1–B.6 for $\mathbf{i} = 2, 3$ and 4

$$\Psi(\mathbf{A2}') = \psi_2 - l\psi_7 - k\psi_8 + kl\psi_9 \quad (\text{B.1})$$

$$\Psi(\mathbf{A2}'') = \psi_2 - k\psi_7 - l\psi_8 + kl\psi_9 \quad (\text{B.2})$$

$$\Psi(\mathbf{A3}') = \psi_3 - l\psi_5 - k\psi_7 + kl\psi_9 \quad (\text{B.3})$$

$$\Psi(\mathbf{A3}'') = \psi_3 - k\psi_5 - l\psi_7 + kl\psi_9 \quad (\text{B.4})$$

$$\Psi(\mathbf{A4}') = \psi_4 - l\psi_6 - k\psi_8 + kl\psi_9 \quad (\text{B.5})$$

$$\Psi(\mathbf{A4}'') = \psi_4 - k\psi_6 - l\psi_8 + kl\psi_9 \quad (\text{B.6})$$

The $N_3\cdot$ radical

With $\Psi(\mathbf{R1}) = \Psi(\mathbf{R1}') + \mu\Psi(\mathbf{R1}'')$ given by Eq. 19, to construct the $\Psi(\mathbf{R2}) = \Psi(\mathbf{R2}') + \mu\Psi(\mathbf{R2}'')$, $\Psi(\mathbf{R3}) = \Psi(\mathbf{R3}') + \nu\Psi(\mathbf{R3}'')$ and $\Psi(\mathbf{R4}) = \Psi(\mathbf{R4}') + \nu\Psi(\mathbf{R4}'')$ for the ground-state of the N_3 radical, we have

$$\Psi(\mathbf{R2}') = \psi_2 - k\psi_6 - l\psi_9 + kl\psi_7 \quad (\text{B.7})$$

$$\Psi(\mathbf{R2}'') = \psi_2 - l\psi_6 - k\psi_9 + kl\psi_7 \quad (\text{B.8})$$

$$\Psi(\mathbf{R3}') = \psi_4 - k\psi_6 - l\psi_{11} + kl\psi_7 \quad (\text{B.9})$$

$$\Psi(\mathbf{R3}'') = \psi_4 - l\psi_6 - k\psi_{11} + kl\psi_7 \quad (\text{B.10})$$

$$\Psi(\mathbf{R4}') = \psi_3 - k\psi_5 - l\psi_{12} + kl\psi_8 \quad (\text{B.11})$$

$$\Psi(\mathbf{R4}'') = \psi_3 - l\psi_5 - k\psi_{12} + kl\psi_8 \quad (\text{B.12})$$

from which we obtain Eq. 22 for the $(\mathbf{R1}) \leftrightarrow \mathbf{R2} \leftrightarrow (\mathbf{R3} \leftrightarrow \mathbf{R4})$ resonance.

Supporting information

Un-normalized coefficients are given as Supporting Information available online (DOI: 10.5560/ZNB.2012-0161).

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