Recent Developments in the Chemistry of Covalent Azides

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The experimental and theoretical chemistry of covalently bound azides is an area that has seen considerable renaissance over the past 10 years. This review is not exhaustive in scope but rather focuses on and highlights certain aspects in this field. In particular, the stability and dissociation of HN_3 is discussed at a very high level of theory (CASSCF and MCSCF-CI) and compared and contrasted with experimental data and results from "medium"-level ab initio computations (MP2, B-LYP). From these results credence is given to those values calculated for larger systems and heavy elements for which very high level computations are not possible. The experimentally well-characterized covalent halogen azides (XN_3, where X = F, Cl, Br, I) as well as the heavy-element group-15 compound $Sb(N_3)_3$ are discussed. The review also includes discussion of the bond properties of the highly unstable N-bound azides $ON-N_3$ and $(FSO_2)_2N-N_3$. In the final chapter attention is drawn to the recently predicted and eventually experimentally verified elusive species OCN−NCO, which is isoelectronic to the hitherto unknown diazide N_6.

The chemistry of covalent inorganic azides originated with the synthesis of aqueous HN_3 solutions by Tony Curtius in 1890[1]. A little later, in 1900, it proved possible to prepare iodine azide, IN_3[2], as the first member of the now complete series of halogen azides. Over the years the structures of several covalently bound azides have been determined experimentally by microwave spectroscopy (MW) or by X-ray (X-ray) or electron diffraction (ED) techniques. Examples are HN_3 (MW)[3a] and $H_2N_3^+$ (X-ray)[3b], NCN_3 (MW)[4], CF_3N_3 (ED, MW)[5], H_3SiN_3 (MW) and H_3GeN_3 (ED)[6], FN_3 (MW) and ClN_3 (MW)[7] as well as $Te(N_3)_3^+$ (X-ray)[8]. Recently the structures of several kinetically stabilized azides have been determined; examples are $(CF_3)As(N_3)_2$ (ED) and $(CF_3)_2AsN_3$ (ED)[9], the gallium complex $(C_5H_5N)_3Ga(N_3)_3$ (X-ray)[10] and the organotellurium azide $(Ph_2TeN_3)_2O$ (X-ray)[11]. A fuller account is given in ref.[12].

It has been our goal to make very simple and highly unstable and reactive classes of compounds that many chemists would consider not preparable based on past experience. We found such to be the case for many covalent azides and related isoelectronic species [e.g. N_4O, R_2N-N_3 and $(OCN)_2$], for which, in spite of several notable recent results (see above), the chemistry, the quantitative bond description and the mechanisms for their decomposition reactions remain poorly understood. Consequently the elucidation of their bond properties, by high-level quantum chemical ab initio computations combined with today's ready access to low-temperature methods such as X-ray diffraction and multinuclear NMR and Raman spectroscopy, became of

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great importance to us. In this context, we have always been interested in the interplay between experimental work, bond theory and conceptual understanding. Although most of our own theoretical work has always been based on MO computations, to give a more balanced approach to the subject a short VB discussion of the bonding in HN_3, ONN_3 and $(OCN)_2$ has been included in this review.

Some Comments on the Theory Applied (A fuller account is given in ref.[13–17])

In the discussion of the azide compounds in this account we use perturbation theory according to Møller–Plesset, which takes higher excitations into account by using a perturbation operator and using Rayleigh–Schrödinger perturbation theory to obtain a better wave function and energies[16,18]. Relativistic effects were always taken into consideration for period four and heavier elements (e.g. Br, I). Quasirelativistic pseudopotentials (ECPs) of the semilocal type were used where the non-relativistic Hamiltonian was corrected (i) for the relativistic mass increase of the inner electrons and (ii) for the (averaged) spin–orbit coupling[19].

Either localized or delocalized bonding models may be more useful for the discussion of chemical phenomena, but they are equivalent in the final analysis. Whereas there is no doubt about the necessity of canonical MOs for the representation of ionization energies (cf. photoelectron spectroscopy), as early as 1931 Hund already stated the necessary conditions for the possibility of bond localization[20,21]. It is more than justified to apply a localization strategy, for example the NBO analysis that was developed by Weinhold et al.[15d], to "translate" the delocalized canonical MOs into the picture of localized bonds and lone pairs as basic units of molecular structure. The NBO analysis transforms the input basis set into localized basis sets:

input basis set → NAOs → NHOs → NBOs → NLMOs
(NHO, natural hybrid orbital; NBO, natural bond orbital; NLMO, natural localized MO)[15d]

The NBO (ϕ^{NBO}) for a localized bond between atoms A and B is formed from directed orthogonal hybrids h_A and h_B which correspond to the Lewis picture and are therefore well adapted to describing the covalently effects in molecules.

$$\phi_{AB}^{NBO} = c_A h_A + c_B h_B \qquad (1)$$

The antibonding NBOs ($\phi^{*,NBO}$), which are unoccupied in the formal Lewis picture, may then be used to describe non-covalency effects.

$$\phi^{*NBO}_{AB} = c_A h_A - c_B h_B \qquad (2)$$

It has been shown that the corrections due to the small occupancies of these antibonds (non-covalent corrections) are usually so small that the energy lowering can be well approximated by simple second-order perturbative expressions (eq. 3)[15d,15g–h]. The role of antibonds can be seen by transforming the occupied canonical MOs to localized molecular orbitals (LMOs) (eq. 4), which then again are fully occupied with exactly two electrons. In other words, the LMO ϕ_{AB}^{LMO} represents the delocalization of a bond orbital ϕ_{AB}^{NBO}, and therefore describes non-covalent interactions in terms of (negative) hyperconjugation.

$$E^{(2)}_{\phi\phi^*} = -2\,\frac{\langle\phi|\mathbf{h}^F|\phi^*\rangle^2}{E_{\phi^*} - E_{\phi}} \quad (\mathbf{h}^F\text{, Fock operator}) \qquad (3)$$

$$\phi_{AB}^{LMO} = \phi_{AB}^{NBO} + \lambda\phi^{*NBO}_{CD} + \ldots \qquad (4)$$

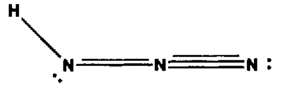
N.B. The VB method only represents a different approach for the description of chemical bond[14]. Initially the method was based on two-center two-electron bonds; however, the increased valence theory (including long bonds and Pauling three-electron bonds) represents a natural extension of the classical concept[22a,b]. Although for quantitative computations the mathematical problem seems to be far more complex, the generalized VB method where the AOs are allowed to vary independently until an energy minimum is reached appears to be little different in the final result from the UHF procedure[22c].

Four-Atomic Covalently Bound Azides: HN_3 and XN_3 (X = F, Cl, Br, I)

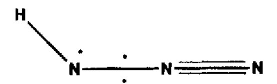
HN_3: The Simplest Azide

When discussing the electronic structure of HN_3, Glukhovtsev and Schleyer have made the sensible distinction between geometric hypervalence and electronic hypervalence[23]. Thus, the calculated (HF/6-31G*//MP2/6-31G*) NN bond lengths in HN_3 of 1.250 (central) and 1.158 (terminal) Å are similar to the calculated values (HF/6-31G*// MP2/6-31G*) of 1.265 and 1.130 Å for the N–N double and triple bonds of HNNH and N_2, respectively[23]. Therefore, HN_3 is an example of a molecule whose bond lengths suggest that the central nitrogen is apparently pentavalent, as indicated in the classical VB structure **I**[24]. However, unless the nitrogen atom expands its valence shell, the π bonds of this structure are fractional electron-pair bonds. The increased-valence structure **II**, with fractional electron-pair bonds and 1-electron bonds, also involves an apparent pentavalence. Some of the properties of these two VB structures can be used to restate the nature of the origin of the apparent electronic pentavalence for nitrogen, namely appreciable contributions of Dewar-type structures such as **III** to the component Lewis structure resonance scheme[24]. Structure **II** is an example of an increased-valence structure[25a–c], and is equivalent to resonance between the canonical Lewis structures **IIIa**, **IIIb**, **IV** and **V**, when the wave functions for the bonds of structure **IV** are formulated using the Heitler–London procedure. When LMOs are used to accommodate the electrons of these bonds, **II** is equivalent to resonance between 25(!) canonical Lewis structures[25d].

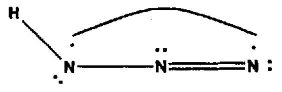
Despite the relatively strong N1–N2 bond in HN_3, thermal fragmentation of this molecule is not induced by breaking the $H-N_3$ bond but rather by dissociation into HN and N_2. Since the electronic ground state of XN (X = H, halogen) is a triplet state ($^3\Sigma^-$), dissociation of XN_3 ($^1A'$) into XN ($^3\Sigma^-$) and N_2 ($^1\Sigma_g^+$) is spin-symmetry forbidden. Nevertheless, pyrolysis experiments have shown that HN_3 decomposes into N_2 and HN in the ground-state triplet ($^3\Sigma^-$) state[26a]. A theoretical study[26b] on the energetics of the dissociation reaction of HN_3 ($^1A'$) yielding N_2 ($^1\Sigma_g^+$) and



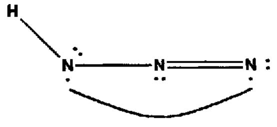
I



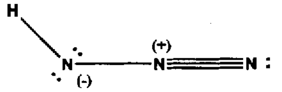
II



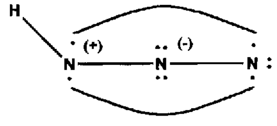
IIIa



IIIb



IV



V

Note: Thin bond lines in structures **I** and **II** represent fractional bonds (cf. ref.[22]).

HN ($^3\Sigma^-$) at a very high level of theory using CASSCF and MCSCF-CI techniques has shown that singlet−triplet coupling occurs because the HN_3 wave function in the region of the transition state can be considered an equal mixture of N_2 (X) · NH ($a^1\Delta$) and N_2 (X) · NH ($b^1\Sigma^+$). The calculated barrier for the dissociation (35.7 kcal mol^{-1}) is in excellent agreement with the value of 36 kcal mol^{-1} estimated from thermal dissociation studies[26c]. This result suggests that the stabilities of XN_3 molecules may be determined by the activation barrier for breaking the $XN-N_2$ bond, which in turn involves singlet−triplet coupling along the reaction course. The accurate calculation of the dissociation barrier of XN_3 yielding XN and N_2 needs a very high level of theory that is not possible for larger atoms or substituent groups X at present time. However, Frenking et al. have shown that for halogen azides XN_3 (X = halogen) the reaction energy of the dissociation reaction of XN_3 ($^1A'$) yielding N_2 ($^1\Sigma_g^+$) and HN ($^3\Sigma^-$) can be calculated at the electron-correlated MP2 level of theory using effective core potentials for the heavy elements MP2/LANL1DZ+P[29a]. Generally, the agreement between the theoretical and experimental data for the heat of formation calculated at the MP2 level (DZ+P basis set) is very good for HN_3[29b]. This gives credence to those calculated dissociation energies for which there are no experimental data due to the extreme lability of the compounds in question, for instance the novel N-oxide $ON-N_3$ (see below).

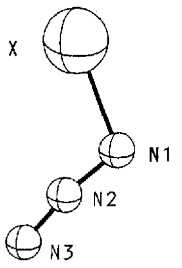
The Halogen Azides

Even then years ago structural data (experimental and theoretical) on covalent azides were very rare due to the explosive nature of these compounds and to limited computer power. In one of the early papers reporting on the experimental structure determination of CF_3N_3, Christe et al. correctly stated that one of the most significant features of the CF_3N_3 structure was the nonlinearity of the N_2 group[5]. The same authors, however, also pointed out that it should be kept in mind that the value of the NNN angle carries a rather large uncertainty[5]. Today we know from experimental and theoretical studies that, in contrast to the azide anion (N_3^-, $D_{\infty h}$), all covalent azides possess a nonlinear azide group, and we can understand or at least rationalize this remarkable structural feature.

There is probably no class of covalent azides that has been studied more comprehensively than the halogen azides. The structures of all members of this XN_3 family (X = F[7a], Cl[7b], Br[27], I[28]) were determined experimentally and were computed at high levels of theory. Among the halogen azides iodine azide is, in terms of its structure and bonding, probably the most studied compound[28]. Experimentally the structure of IN_3 was determined in the solid state (X-ray)[28a] as well as in the gas phase (ED, MW)[28b,c] and several ab initio and DFT computations have been reported[28a,29].

HN_3 and halogen azides XN1N2N3 (X = F, Cl, Br, I) present as discrete monomeric species in the gas phase display a bent *trans* C_s configuration with an N1−N2−N3 bond angle of 172 ± 3°, and two significantly different N−N bond lengths (N1−N2 1.24 ± 0.02 Å, N2−N3 1.160 ± 0.005 Å, Figure 1). Generally, the agreement between the experimental and computed data is good. It proved to be very helpful to introduce quasirelativistic pseudopotentials for the heavy halogens Br and I to account for relativistic effects. For instance, calculations utilizing an effective core potential often led to better results in less time than all-electron computations[12a]. Table 1 shows the average differences between the experimentally observed and computed structural parameters for the halogen azides. Usually ab initio HF calculations give bond distances that are too short, whereas DFT computations predict distances that are somewhat too long. It can be concluded that the uncorrelated ab initio (HF) and DFT (B) calculations are of similar quality. The density functional computation usually gives better bond angles but the HF method results in better distances and vice versa. On correlated levels both methods − ab initio (MP2) and DFT (B-LYP) − compare nicely with the experimental data[29b].

Figure 1. Depiction of a covalent XN_3 azide in the *trans-bent* C_s conformation



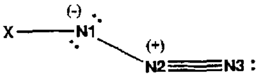
At this stage we know that among the four-atomic XN_3 species there is excellent agreement between computed and experimentally observed structural parameters. Undoubtedly the N_3 unit is bent and there are always two different N−N bond lengths (cf. VB discussion of HN_3, see above). But how can we explain these features? The localization

Table 1. Average deviations of ab initio and DFT-computed structural parameters of four-atomic covalent azides XN_3 (X = H, F, Cl, Br, I) from the experimentally observed data[29b]

	HF [a]	MP2 [a]	B [b]	BLYP [b, c]
Δr (Å)	0.03	0.03	0.06	0.03
Δ< (°)	2.8	1.5	1.5	1.5

[a] LANL1DZ+P. – [b] ECPs for Cl, Br, I: [5s5p1d](3s3p1d)-DZ+P; basis set: 6-31+G*. – [c] "B" denotes Becke's 1988 functional, which includes the Slater exchange along with correlation including the gradient of the density[36].

procedure of covalent XN_3 azides results in an NBO analysis that yields the configuration **VI** as the energetically most favorable Lewis structure. According to this, there is a single bond between N1 and N2 and a triple bond between N2 and N3.



VI

Whereas the observed values for the N2−N3 bond really correspond to a (weak) triple bond, the N1−N2 bond in terms of its length resembles rather more a double than a single bond (typical experimental values: N−N single bond, 1.449 Å; N=N double bond, 1.252 Å; N≡N triple bond, 1.098 Å)[30]. If we now allow for the non-covalent effects that are ignored in the "natural" Lewis picture by a second-order perturbation calculation, two significant results can be obtained: (i) The most important non-covalent contributions in the XN_3 system are the π-delocalization over the entire molecule (resonance). This explains the planarity of the molecule (i.e. C_s symmetry). (ii) There is a strong negative hyperconjugation (intramolecular donor−acceptor interaction; for the exact definition and an early study on *negative hyperconjugation*, see ref.[15g,h]), which donates electron density from the filled $\sigma(X-N1)$ orbital into the unfilled, antibonding $\pi^*(N2-N3)$ orbital (Figure 2). This weakens the X−N1 and N2−N3 bonds, while it strengthens the N1−N2 bond. Morevoer, from the pictorial approach of the orbitals shown in Figure 2 one can see that a *trans-bent* conformation favors the hyperconjugative $\sigma(X-N1) \rightarrow \pi^*(N2-N3)$ overlap. (A VB rationalization for the N1−N2−N3 bending is provided in Table 1 of ref.[33].)

Table 2 lists the linear NLMO bond orders for XN_3 azides. It is noteworthy that the total bond order (ΣBO) at the central N2 atom is significantly greater than 3 in all cases, which nicely corresponds with the VB discussion of HN_3 (see above).

Two N-Bound Azides: $ON-N_3$ and $(FSO_2)_2N-N_3$

Suitable correlations of experimental and quantum mechanical molecular data together with calculations of energy hypersurfaces make it possible to estimate the structures of short-lived molecules that cannot be isolated on the preparative scale[12a,31]. Every defined molecular state possesses a certain structure, and changes in its energy or charge distribution cause structural changes that occur through the molecule's specific molecular dynamics.

Figure 2. Negative $\sigma(X-N1) \rightarrow \pi^*(N2-N3)$ hyperconjugation in XN_3

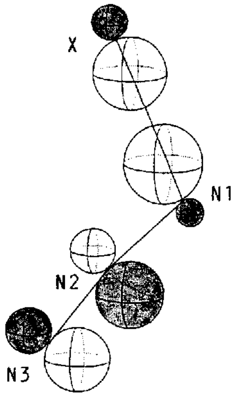


Table 2. Linear NLMO bond orders (BO), overall bond orders (ΣBO) and NPA charges q (in e) for covalent XN_3 molecules[a],[12a]

	BO (X–N1)	BO(N1–N2)	BO(N2–N3)	ΣBO(N1)	ΣBO(N2)	ΣBO(N3)
HN_3	0.60	1.11	2.41	1.43	3.54	2.11
FN_3	0.67	1.06	2.30	1.52	3.34	2.08
ClN_3	0.90	1.09	2.38	1.76	3.47	2.12
BrN_3	0.79	1.10	2.38	1.65	3.50	2.10
IN_3	0.67	1.12	2.39	1.65	3.50	2.10
ONN_3	0.99	0.99	2.52	1.70	3.54	2.29
O_2NN_3	0.92	0.97	2.50	1.56	3.48	2.30
	q (X)	q (N1)	q (N2)	q (N3)		
HN_3	+0.40	–0.67	+0.30	–0.03		
FN_3	–0.29	–0.03	+0.23	–0.29		
ClN_3	+0.12	–0.45	+0.29	–0.12		
BrN_3	+0.21	–0.54	+0.29	–0.21		
IN_3	+0.34	–0.62	+0.29	–0.00		
ONN_3	O –0.34 N4 +0.29	–0.35	+0.29	+0.12		

[a] Basis set: HF/6-31+G* for Cl, Br, I; ECPs, basis set: [5s5p1d]/(3s3p1d)-(DZ+P).

The decomposition of the unstable nitrosyl azide, $ON-N_3$, which is intrinsically stable at 0 K and, according to experiments, also at T = 180 K, will be used as an example[32,33]. N_4O was shown by Raman spectroscopy to have an open-chain C_s structure with a *trans-trans* arrangement at N1−N4 and N1−N2 (Figure 3)[32]. The MP2-predicted N1−N4 bond length of 1.48 Å (i.e. the $ON-N_3$ bond) is longer than the N−N bond length in N_2H_4 (1.45 Å)[34a] but much shorter than the N−N bond length in the weakly bound O_2N-NO_2 (1.78 Å)[34b], and resembles the bond length in F_2N-NF_2 (1.49 Å)[34c]. This $ON-N_3$ bond has a polarity $ON^{\delta+}-^{\delta-}N_3$ (NBO charges: O −0.34, N4 +0.29, N1 −0.35, N2 +0.29, N3 +0.12). In contrast, the O−N4 bond is quite short (1.20 Å) and lies close to N_2O (1.19 Å)[34d]. Both features can be understood if we now allow for the non-covalent effects which are ignored in the "natural" Lewis picture (cf. structure **VII**) by a second-order perturbation calculation[32]. N_4O shows a strong negative hyperconjugation in the way that electron density is donated from one of the p lone pairs (p-LP) of the oxygen atom into the unfilled and antibonding σ^*(N4-N1) orbital (Figure 4). This intramolecular donor–acceptor interaction simultaneously strengthens the O–N4 bond and weakens the N1–N4 bond. [N.B. In halogen azides XN_3 the strongest hyperconjugation is of the type $\sigma \rightarrow \pi^*$, whereas in N_4O it is of the type LP→σ^*; both, however, are negative hyperconjugations (cf. ref.[15g,h]).] In a very recent paper Galbraith and Schaeffer III[35] confirmed our previous results[32] using the far better (and more expensive) triple-ζ plus double-polarization single and double excitation-coupled cluster (TZ2P CCSD) method and the multireference configuration interaction method (MRCISD)[35]. They predicted an O–N4 bond length of 1.18 Å and an N1–N4 length of 1.47 Å, which is nicely in agreement with our earlier work on MP2 level (6-31+G* basis set)[32].

Figure 3. MP2 computed structure of N_4O: *trans-trans* isomer (left) and *cis-cis* isomer (right)

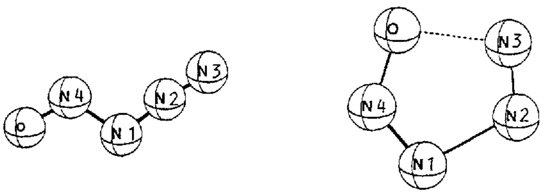
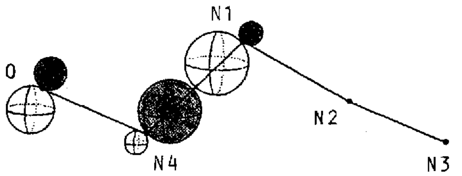


Figure 4. Negative hyperconjugation LP(O) → σ^*(N4–N1) in N_4O



The N_4O molecule has two possible modes of unimolecular decay[32]. On the one hand, rotation around the N1–N4 axis can lead to the *cis-cis* isomer (very shallow minimum on the MP2 level but not at the TZ2P CCSD level; Figures 3 and 5; cf. structure **IX**), which then decomposes, according to the hypersurface shown in Figure 6, via cyclic N_4O (minimum on all levels of theory applied; cf. structure **X**) into N_2O and N_2. On the other hand, the *trans-trans* isomer can also fragment directly by a change in the N1–N2 distance (Figure 7). The rotation into the *cis-cis* isomer, however, has a calculated barrier of 7 kcal mol^{-1} (Figure 5), whereas the transition state for the N1–N2 variation lies 24 kcal mol^{-1} in energy above the *trans-trans* isomer. This indicates that a unimolecular fragmentation into N_2O and N_2 is more likely to occur via *cis-cis* N_4O and cyclic N_4O. The calculated potential energy surface for the decomposition without the rotation (Figure 7) shows that *trans-trans* N_4O does not lead to linear N_2O but rather to cyclic N_2O (cf. structure **VIII**). The hypersurface depicted in Figure 7 shows three minima: *trans-trans* N_4O, $C_{\infty v}$-N_2O + N_2, and C_{2v}-N_2O + N_2. Hence *trans-trans* N_4O can decompose not only by the pathway initiated by the rotation into the *cis-cis* isomer, but also by two additional pathways.

Figure 5. Rotational barrier for the *cis-cis*→*trans-trans* isomerization of N_4O (ω = O–N4–N1–N2)

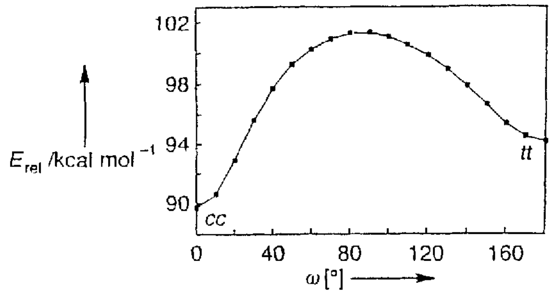


Figure 6. Two-dimensional MP2 energy hypersurface for the decomposition of *cis-cis* N_4O; a: *cis-cis* N_4O, b: cyclic N_4O, c: linear N_2O + N_2

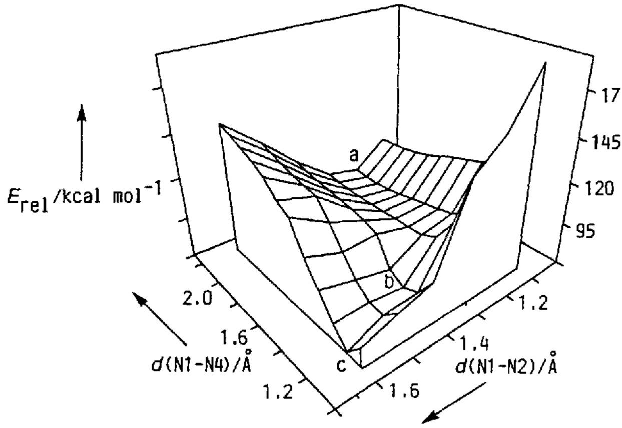
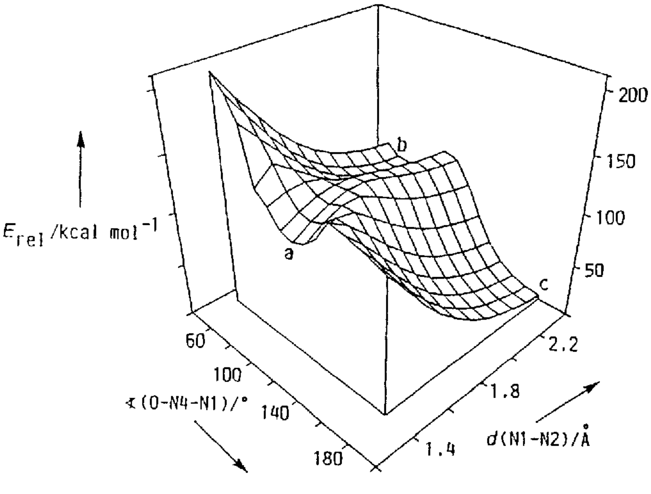
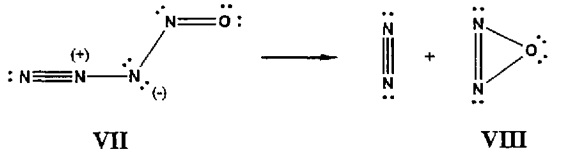


Figure 7. Two-dimensional MP2 energy hypersurface for the decomposition of *trans-trans* N_4O; a: *trans-trans* N_4O, b: cyclic N_2O + N_2, c: linear N_2O + N_2

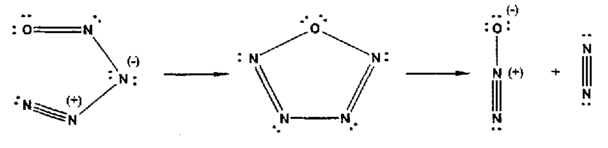


Recently the decomposition of N_4O has been studied on the basis of VB representations[33]. Standard Lewis and increased-valence structures were used for this purpose. A standard Lewis-type VB formulation for the dissociation of the *trans-trans* N_4O (**VII**) to form cyclic N_2O (**VIII**) and N_2 is given in eq. 5. The other (more likely) decomposition pathway for N_4O involves interconversion of *trans-trans*

N_4O into *cis-cis* N_4O (**IX**), which then generates cyclic N_4O (**X**) as an intermediate species. Kekulé–Lewis and increased-valence representations for the *cis-cis* N_4O decomposition are indicated in eq. 6 and Scheme 1. (N.B. Structure **VII** represents the Lewis-type VB structure for N_4O whereas structure **XI** represents the increased-valence structure for N_4O.)

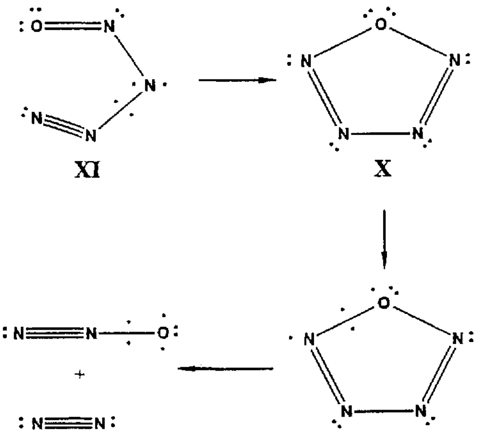

(5)

VII **VIII**


(6)

IX **X**

Scheme 1. Unimolecular decomposition of *trans-trans* N_4O via *cis-cis* N_4O and N_2



Chlorine azide, ClN_3, is known to be one of the most stable halogen azides[12a]. The "chlorine-like" $N(SO_2F)_2$ radical resembles the Cl atom in valency and approximate group electronegativity[37a]. Consequently, $(FSO_2)_2N-N_3$ was prepared and identified from its high-resolution mass spectrum and characterized by IR, Raman and multinuclear NMR data[37a].

The structure of $(FSO_2)_2N-N_3$ was computed ab initio (Figure 8) and, not unexpectedly, shows all characteristic features of a covalent azide species: (i) a long and weak N4–N1 bond with a length of 1.409 Å; (ii) two significantly different N–N azide bond lengths between N1–N2 (1.285 Å) and N2–N3 (1.087 Å); (iii) a bent N_3 unit with an N2N3N4 angle of 172.1°[37a].

Figure 8. RHF/6-31G(d,p) optimized structure of $(FSO_2)_2N-N_3$ including NPA charges

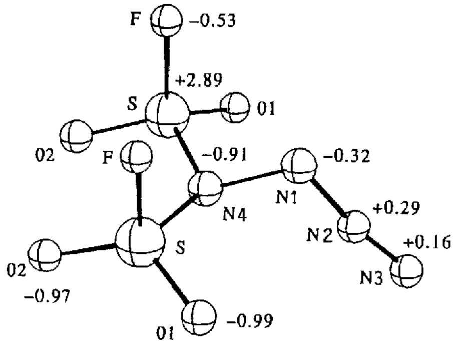
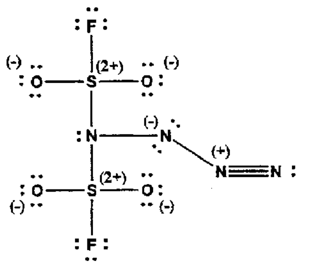
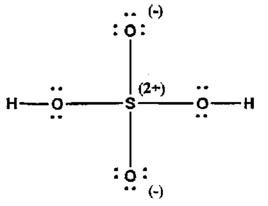


Figure 8 also contains the NPA charges calculated for $(FSO_2)_2N-N_3$. It can be seen that the molecule is best represented by the semipolar formulation **XII**. The backbonding that is superimposed on this semipolar structure is difficult to depict in a structural formula. [N.B. Also sulfuric acid, H_2SO_4, is better represented by structure **XIII** than by a structure with wo S=O double bonds; the same is of course true for SO_2 and SO_3.][15b,16,38]



XII



XIII

$Sb(N_3)_3$, An Analogue of the Hitherto Unknown Nitrogen Triazide $N(N_3)$, and $(OCN)_2$, An Analogue of the Hitherto Unknown Diazide, N_3-N_3

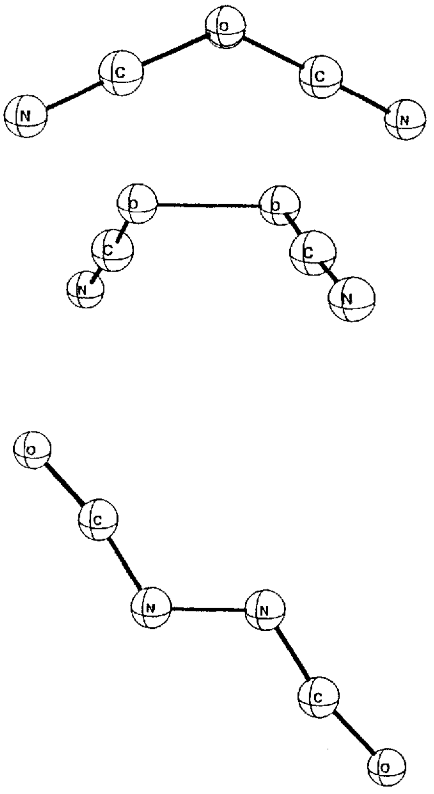
A long-term goal of all azide chemists, the preparation of nitrogen triazide, $N(N_3)_3$, has not been achieved to date[37,39a]. However, ab initio MO and DFT calculations show that azidamines, a new family of polynitrogen compounds, have minima on their respective potential energy surfaces[39b]. Quite recently the geometries, vibrational frequencies, and heats of formation have been predicted for $N(N_3)_3$, $HN(N_3)_2$, the $N(N_3)_2^-$ anion, and the $N(N_3)_4^+$ cation[39b]. All of these compounds are highly energetic materials with large positive heats of formation. Compounds that are isovalent to $N(N_3)_3$, however, $E(N_3)_3$ (E = P, As, Sb)[40–42] have been made and $Sb(N_3)_3$ was studied theoretically[42]. An interesting, though not unexpected, structural feature of $Sb(N_3)_3$ is undoubtedly the N–Sb–N bond angle of 93° [for comparison, the HF-computed valence angle in $N(N_3)_3$ is 106.7°][37b]. This can best be explained by a less-effective isovalent hybridization for elements of higher main groups (Sb) compared to elements of the first row (N)[43,44].

Even though the chemistry of the N_3 group can frequently be explained by using the pseudohalogen concept, it has not been possible to date to observe the species analogous to Cl_2, namely $N_3{-}N_3$. It is unlikely, however, that such a molecule would be in any way kinetically stabilized[23,39a].

In a combined experimental (IR, low-temperature ^{14}N NMR) and theoretical ab initio study we recently investigated the reaction of AgOCN with Br_2[45]. The intermediate formation of OCN–NCO (**XI**), the isoelectronic analogue of N_6, was observed. No evidence for the formation of NCO–OCN (**XII**) was found. (N.B. Quite recently ONC–CNO, formally a structural isomer of **XI**, was also detected[46].)

To answer the question of why **XIV** and not **XV** is formed as a short-lived intermediate by the reaction of AgOCN with Br_2, we carried out ab initio computations[45]. The structures of both isomers were computed and fully optimized at the MP2(FU)/6-31G(d) level (Figure 9). The N–N bound species **XIV** turned out to be favored over the O–O isomer **XV** by 82.1 kcal mol^{-1} at the MP2 level.

Figure 9. MP2 optimized structures; top: two different views of NCO–OCN (**XV**, see below); bottom: OCN–NCO (**XIV**, see below)



The very long and weak O–O bond in **XV**, with 1.62 Å [cf. d(O–O, H_2O_2) = 1.47 Å][1], is in contrast to the relatively short N–N bond in **XIV**, with 1.39 Å. The latter value of the N–N distance corresponds to a bond order between a single and a double bond (typical experimental values: N–N single bond, 1.449 Å, N=N double bond, 1.252 Å)[30]. These rather special bonding situations can be rationalized in the NBO picture by strong non-covalent contributions. In the case of the O–O compound (**XV**) there are two strong intramolecular donor–acceptor interactions that both weaken the O–O bond and therefore also explain the long O–O distance. In one interaction electron density is transferred from the bonding π(CN) orbitals into the empty and antibonding σ^*(OO) orbital (Figure 10a). In the other interaction electron density flows from the occupied σ(OO) orbital into the empty and antibonding π^*(CN) orbitals (Figure 10b). In contrast to this situation the N–N compound (**XIV**) only shows one strong hyperconjugation with a donation of electron density from the π(C1N1) orbital into the π^*(C2N2) orbital [and vice versa: $\pi(C2N2) \rightarrow \pi^*(C1N1)$]. This interaction clearly strengthens the N–N bond (Figure 11) and therefore accounts for its partial double-bond character.

Figure 10. Negative hyperconjugation in NCO–OCN (**XV**); top: $2 \times \pi(CN) \rightarrow \sigma^*(OO)$, bottom: $\sigma(OO) \rightarrow \pi^*(CN)$

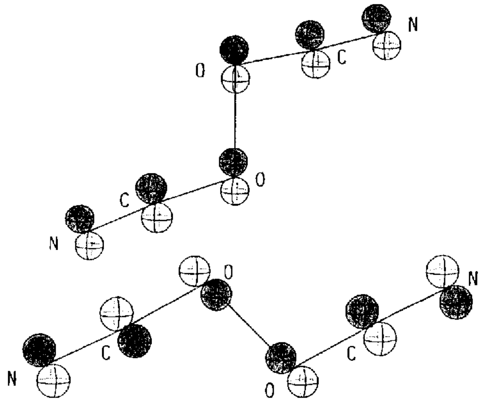
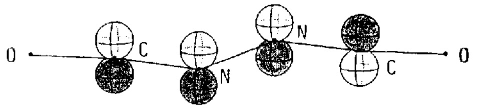
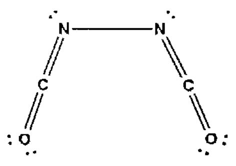
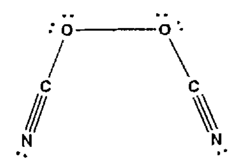


Figure 11. Negative hyperconjugation in OCN–NCO (**XIV**): $\pi(C1N1) \rightarrow \pi^*(C2N2)$ [same for: $\pi(C2N2) \rightarrow \pi^*(C1N1)$]




XIV


XV

In VB terms the preference for the N–N bound isomer **XIV** over the O–O compound **XV** can be explained either by the preferred localization of the single electron in the radical intermediate OCN$^•$ in a nitrogen AO or by the fact that lone pair–lone pair repulsion favors compound **XIV** (*one* LP per N atom) over compound **XV** (*two* LPs per O atom) (cf. dissociation energies: HO–OH, 34.5 kcal mol^{-1}; $H_2N{-}NH_2$, 59.1 kcal mol^{-1})[47]. The calculated geometry for the OCN radical [d(NC) = 1.23 Å, d(CO) = 1.13 Å][48] is also in better accord with a Lewis structure of the type $^•N{=}C{=}O$ than with type $N{\equiv}C{-}O^•$[48]. These considerations clearly suggest that structure **XIV** should be preferred over structure **XV**. It is of interest to note that by changing the spin pairings for the π-electrons of the C=N bonds of VB structure **XIV**, one obtains a N−N π bond and a long C−C π bond. Such a structure corresponds to the Dewar-type structure of butadiene, and helps to account for the calculated shortening of the N−N bond relative to a single bond (see above).

Quite recently, in an independent theoretical and experimental study, G. Maier et al. succeeded for the first time in isolating the predicted NCO−OCN molecule from the photolysis reaction of carbonyl azide isocyanate (eq. 7) in an argon matrix at 10 K[50].

$$N_3{-}C(O){-}N{=}C{=}O \xrightarrow{h\nu,\ 10K} O{=}C{=}N{-}N{=}C{=}O + N_2 \tag{7}$$

Conclusions

The chemistry of covalent azides is an experimentally exciting (you are always dealing with thermally highly unstable and usually explosive materials) and theoretically stimulating area of research, where a real and mutual stimulation between theory and experiment takes place constantly.

The access to powerful computers, convenient computational program packages and last but not least the availability of quasirelativistic pseudopotentials for all main group elements made this research possible[19c]. The handling of these usually highly explosive materials in the lab still requires great skills from the experimentalist. However, modern techniques such as low-temperature IR, Raman and NMR spectroscopy as well as low-temperature X-ray diffraction methods and electron-diffraction studies or microwave spectroscopy in the gas phase have made it possible to obtain experimental structural data for a comparison with the ab initio computed results.

Not only can we now describe, understand and predict(!) all significant structural features of covalent azides, but with the help of modern quantum theory we can translate the results derived from MO computations (canonical MOs) into the more familiar localized Lewis picture (NBO analysis) where non-covalent contributions (delocalization effects) can directly be seen from the nature of the NLMOs (natural localized MOs). The concept of (negative) hyperconjugation clearly accounts for many unusual structural features in this class of compounds (cf. ref.[15g,h]). In a way one can state that localization strategies bridge the (in reality probably nonexistent) gap between MO and VB theory. Some examples from increased-valence studies highlighted how easily this theory can also be used in a qualitative manner rather than just being suitable for high-school education.

Now that the question about structure and bonding in covalent azides appears to be answered to a certain extent, we wish to use the ab initio methods also as a predictive tool to search for even more unusual non-metal compounds that may be seen as the hypothetical combination of azide radicals with other isoelectronic (or just pseudohalogen) radicals. A first example of this type of work was given in the detection of OCN−NCO[45,50], which for years was thought to be NCO−OCN[49].

Update

While this review was with the referees and in processing we and others have been able to finish and publish experimental and theoretical work on $(CF_3)_3GeN_3$[51a], N_4S[51b,c], BrN_3[51d], $FXeN_3$[51e], and $N_5{-}N_3$[51f].

This review would not have been possible without the fine, dedicated experimental and theoretical work of former and present graduate students and postdoctoral fellows, especially of Dr. *Inis C. Tornieporth-Oetting*, whose outstanding work opened up this field, and Dr. *Axel Schulz*, who computed many of the molecular structures and bond properties. We thank Dr. *Peter S. White* for X-ray structure determinations, Professor *István Hargittai* and Professor *Magdolna Hargittai* for electron diffraction studies and Professor *Richard D. Harcourt* for many spirited discussions. I also thank a referee for pointing out one important missed literature citation. This study was supported in part by the University of Glasgow, the DFG, the FCI and NATO [TMK, PSW CRG 920034/1−3].

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