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Transition-Metal Nitrides, Organic Polyenes, and Phosphazenes: A Structural and Orbital Analogy

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Abstract: M–N distances in d^0 transition-metal nitrides parallel C–C bond lengths in linear and cyclic hydrocarbon polyenes. The structural similarity can be traced to the similar π systems of the known nitrides and their polyene analogues: allyl and pentadienyl cations, as well as polyacetylene and cyclooctatetraene. We find that cyclic delocalization of its in-plane π electrons should stabilize the as yet unknown benzene analogue $(L_nMoN)_3$. However, it is not certain that this system will have all equal MN bond lengths. The tendency in cyclic $(L_nMoN)_4$ to localize bonds or alternate bond lengths can be traced to a heteromorphic in-plane π system and the efficient operation of a second-order Jahn–Teller mixing of its nondegenerate, nonbonding π orbitals. In the corresponding tetrameric cyclic phosphazene the relevant in-plane P- and N-based orbitals are much more split in energy, and the driving force for localization is much diminished.

Early transition-metal nitrides come in a large variety of geometries and states of aggregation, exemplified by the monomer **1**, the binuclear mononitride **2**, the trinuclear dinitride **3**, the tetramer **4**, and the polymer **5**.[1] **2** has symmetrical and **3** nearly symmetrical metal-nitrogen bonding, whereas **4** and **5** are clearly highly asymmetric with strongly alternating MoN bond lengths.

This is not an accident. Neither is the obvious resemblance of these molecules to ethylene (or acetylene), allyl and pentadienyl cations, cyclooctatetraene, and an infinite polyene or polyacetylene. This appealing analogy and some of its less obvious aspects will be investigated in this paper. The analogy is presented for the nitrides, but complexes bridged by other main group atoms[19] must have π systems similar to the polyene orbitals. The structural resemblance to the polyenes is greatest when the electronegativity difference between metal and bridging atom is small, as it is for the nitrides.

First let us put forward the reason for an analogy. Each of the molecules **1–5** could be viewed as a d^0 complex (Ta(V), W(VI), Re(VII)) if the nitride is taken as N^{3-}. This is just a formalism, as everyone recognizes, but it is a convenient starting point. It allows one to see clearly these molecules as chains or rings with two perpendicular π systems, made up of alternating metal and N atoms, and carrying as many electron pairs as there are nitrides. One of the representative π systems (no phases yet) is shown in **6**, and the other is at right angles to it. The π system of the tetramer is a little different; we have discussed it elsewhere,[2] and will do so again below.

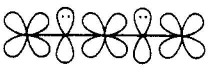
6


Table I. Tungsten–Nitrogen Distances Representative of Single, Double, and Triple Bonds between Nitrogen and a Third-Row Transition-Metal Atom

bond type	d_{M-N} (Å)	compd	ref
single			
$M—NR_3$	2.24	$(\eta^5\text{-}C_5H_5)W(NH_2Me)\text{-}(CO)_2(CONHMe)$	3a
$M—NML_n$	2.10–2.15	$(WNCl_3)_4 0.5HN_3$; $(WNCl_3POCl_3)_4$	3b
double			
$M{=}NR_2$	1.92	$W(NMe_2)_3(O_2CNMe_2)_3$	3c
$M{=}NML_n$	1.84	$W_2NCl_{10}^-$	3d
triple			
$M\equiv NR$	1.71	$W_2Cl_6(NR)_2(\mu\text{-}Cl)_2$	3e
$M\equiv N$	1.68	$(WNCl_3)_4 0.5HN_3$; $(WNCl_3POCl_3)_4$	3b

If we have such a general $(ML_n)_xN_y$ oligomer or polymer, it will have two perpendicular π systems (please put aside, for a moment, the nagging question of topology) composed of $x + y$ orbitals, with $2y$ electrons in each. This is just what the single

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[†] Cornell University.
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(1) Dehnicke, K.; Strähle, J. *Angew. Chem.* **1981**, *93*, 451; *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 413. (b) Griffith, W. P. *Coord. Chem. Rev.* **1972**, *8*, 369. (c) Godemeyer, T.; Dehnicke, K.; Fenske, D. *Z. Naturforsch.* **1985**, *B40*, 1005. (d) Schrock, R. R.; Listemann, M. L.; Sturgeoff, L. G. *J. Am. Chem. Soc.* **1982**, *104*, 4291. (e) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Inorg. Chem.* **1983**, *22*, 2903. (f) The molybdenum polymer $^1_\infty[(t\text{-BuO})_3Mo{\equiv}N]$ has only recently been made: Chan, D. M.-T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Marchant, N. S., private communication. Mo–N distances are 1.66 and 2.86 Å in the one-dimensional chain of this complex. (g) Hermann, W. A. *Angew. Chem.* **1986**, *98*, 57; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 56.

(2) Wheeler, R. A.; Whangbo, M.-H.; Hughbanks, T.; Hoffmann, R.; Burdett, J. K.; Albright, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 2222.

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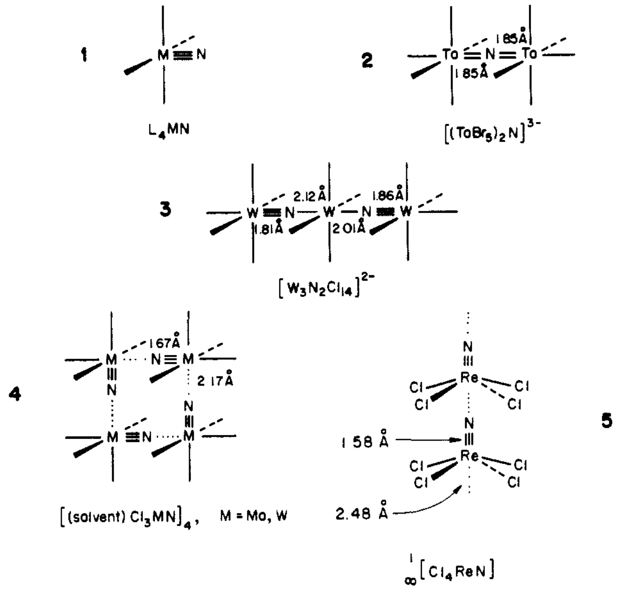
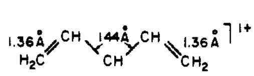
Chart I



π systems of planar allyl cation, pentadienyl cation, cyclooctatetraene, and polyacetylene have.

The question of orbital topology will not go away. But let us delay bringing it up a little longer and examine the structural evidence for the analogy. It is reasonably clear what single, double, and triple C–C bond lengths are. What about for the nitrides? Table I lists typical distances for tungsten–nitrogen single, double, and triple bonds for calibration.[3] Comparing the bond lengths in **2** with those in the table shows that the two equal Ta–N distances in $[(TaBr_5)_2N]^{3-}$ correspond approximately to double bonds. Similarly, the allyl cation is calculated to have equal C–C bond lengths of 1.37 Å,[4] slightly longer than the double bond in ethylene. No experimental bond lengths are available, to our knowledge, for the allyl cation, but IR, NMR, and UV spectral data are consistent with C_{2v} symmetry.[5] Tungsten–nitrogen bond lengths in $[W_3N_2Cl_{14}]^{2-}$, **3**, mirror the pattern of short and long C–C bonds calculated for the pentadienyl cation shown in **7**.[4a] Terminal W–N bonds, the shortest in the molecule, have a length intermediate between a double and a triple bond. Interior W–N bonds are also intermediate in length. They are long, but not as long as the single bond distance in Table I. An experimental estimate of pentadienyl cation bond lengths is also available from the X-ray structure of the heptamethylbenzenonium cation, **8**.[6]



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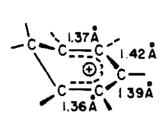


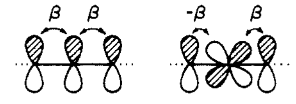
8

The pattern of alternating triple and single bonds in $[Cl_3W\text{-}N{\cdot}OPCl_3]_4$, **4**, parallels the short–long sequence found in many, many nonplanar cyclooctatetraenes. Bond alternation has also been calculated[4c,d] and experimentally inferred[7] for a planar cyclooctatetraene.

That bond lengths should alternate in a long-chain polyene has been clear for some time, from the pioneering studies of Salem and Longuet-Higgins.[8] NMR and X-ray data provide experimental confirmation that bond alternation like that in **5** also occurs in polyacetylene.[9]

So the analogy holds up well structurally. One wants to extend it immediately and inquire where the metal nitride analogues of benzene and cyclobutadiene are, but before we do that let us return to the theoretical underpinnings of the analogy.

A simple Hückel treatment is sufficient to show the similarity between the π systems of odd, linear polyenes and straight-chain transition-metal nitrides. For the polyene chain, AO phases can always be chosen as shown in **9a**, so that the overlap is positive and β negative. Interpolating a d orbital between two p orbitals of **9a** gives the orbital topology shown in **9b**. The d orbital's nodal plane perpendicular to the chain axis changes the sign of one resonance integral. Craig has called π systems in which AO types alternate, heteromorphic, and those containing AO's of the same local symmetry, homomorphic.[10a–d] The Hückel result for the energy levels of an N atom heteromorphic nitride chain is easily shown to be[10e,f]



a **9** b

$$\epsilon_0 = \alpha_M,$$

$$\epsilon_j = \frac{(\alpha_M + \alpha_N) \pm \left((\alpha_M - \alpha_N)^2 + 16\,\beta^2 \sin^2\frac{j\pi}{N+1}\right)^{1/2}}{2} \qquad (1)$$

$$j = 1, 2, ..., (N - 1)/2$$

In this case, α_N is the Coulomb integral for a nitrogen p orbital and α_M is that for the appropriate MX_n fragment orbital.

We should emphasize that the similarity between the energy levels of the linear nitrides and polyenes results from the formal resemblance of their Hückel matrices. For branched molecules, the similarity vanishes. Moreover, angular deviations from the ideal linear chain affect β for the nitrides,[10d] but not for the polyenes. This will become more apparent when we discuss the cyclic compounds.

Equation 1 shows that the orthogonal π systems of the linear nitrides have a nonbonding orbital concentrated on the MX_n fragments analogous to the nonbonding orbital of the linear, odd polyenes.[11] π bonding and antibonding levels of the nitrides are symmetrically disposed about $(\alpha_M + \alpha_N)/2$ in the same way that polyene bonding and antibonding levels are located at $2\beta \cos [j\pi/(N + 1)]$ above and below the energy level of an isolated carbon p orbital, α_c. **10** compares the orbitals of the allyl cation with those of $[(TaBr_5)_2N]^{3-}$. Hückel energies are also shown,

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(3) (a) Adams, R. D.; Chodosh, D. F.; Golembeski, N. M. *Inorg. Chem.* **1978**, *17*, 266. (b) Walker, I.; Strähle, J.; Ruschke, P.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1982**, *487*, 26. Musterle, W.; Strähle, J.; Liebelt, W.; Dehnicke, K. *Z. Naturforsch.* **1979**, *B34*, 942. (c) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 782. (d) Godemeyer, T.; Berg, A.; Gross, H.-D.; Müller, U.; Dehnicke, K. *Z. Naturforsch.* **1985**, *B40*, 999. (e) Drew, M. G. B.; Fowles, G. W. A.; Rice, D. A.; Rolfe, N. *J. Chem. Soc., Chem. Commun.* **1971**, 231.

(4) (a) Truong, T.; Gordon, M. S.; Boudjouk, P. *Organometallics* **1984**, *3*, 484. (b) Lien, M. H.; Hopkinson, A. C. *J. Phys. Chem.* **1984**, *88*, 1513. (c) Dewar, M. J. S.; Merz, K. M., Jr. *J. Phys. Chem.* **1985**, *89*, 4739. (d) Wipff, G.; Wahlgren, U.; Kochanski, E.; Lehn, J. M. *Chem. Phys. Lett.* **1971**, *11*, 350.

(5) Deno, N. C. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1970; Vol. II, p 785.

(6) Baenziger, N. C.; Nelson, A. D. *J. Am. Chem. Soc.* **1968**, *90*, 6602.

(7) (a) Anet, F. A. L.; Bourn, A. J. R.; Lin, Y. S. *J. Am. Chem. Soc.* **1964**, *86*, 3576. (b) Paquette, L. A. *Pure Appl. Chem.* **1982**, *54*, 987. (c) Fray, G. I.; Saxton, R. G. *The Chemistry of Cyclooctatetraene and its Derivatives*; Cambridge University: Cambridge, 1978.

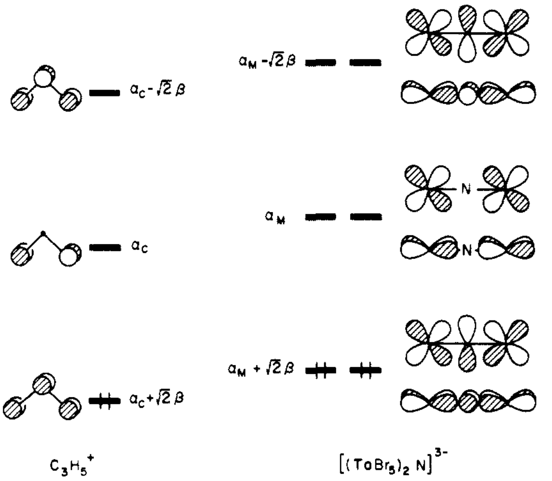
(8) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc.* (*London*) **1959**, *A251*, 172.

(9) (a) Yannoni, C. S.; Clarke, T. C. *Phys. Rev. Lett.* **1983**, *51*, 1191. (b) Fincher, C. R., Jr.; Chen, C.-E.; Heeger, A. J.; MacDiarmid, A. G.; Hastings, J. B. *Phys. Rev. Lett.* **1982**, *48*, 100. (c) Bond alternation in polyacetylene is consistent with a variety of physical measurements, see: Tanaka, K.; Yamabe, T. *Adv. Quant. Chem.* **1985**, *17*, 251 and reference therein.

(10) (a) Craig, D. P. *J. Chem. Soc.* (*London*) **1959**, 997. (b) Mason, S. F. *Nature* (*London*) **1965**, *205*, 495. (c) Magnusson, E. A. *Nature* (*Phys. Sci.*) **1971**, *229*, 176. (d) Häfelinger, G. *Fortschr. Forsch.* **1972**, *28*, 1. (e) Coulson, C. A. *Proc. R. Soc.* (*London*) **1938**, *A164*, 383. (f) Rutherford, D. E. *Proc. R. Soc.* (*Edinburgh*) **1946–1947**, *62*, 229.

(11) Polyene orbitals are described in many excellent books such as the following: (a) Salem, L. *Molecular Orbital Theory of Conjugated Systems*; W. A. Benjamin, Inc.: New York, 1966. (b) Heilbronner, E.; Bock, H. *Das HMO Modell und Seine Anwendung*; Verlag Chemie: Weinheim, 1968.

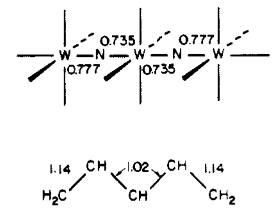
assuming $\alpha_N = \alpha_M$ ($>\alpha_C$). For the nitride, four metal d and two nitrogen p orbitals combine to form two orthogonal sets of π bonding, nonbonding, and π antibonding orbitals analogous to the π orbitals of $C_3H_5^+$. For both molecules only the bonding orbitals are doubly occupied so that the π systems introduce no tendency to distort. Extended Hückel calculations on $[(WCl_5)_2N]^-$ with a constant metal–metal distance give a shallow energy surface for nitrogen atom motion along the W–W axis. The minimum energy occurs for equal W–N bond lengths. Of the known nitrido-bridged transition-metal dimers, only the compounds $[(WCl_5)_2N]^{2-,1-}$, which we would also predict to be symmetrical, are reported to have asymmetrical metal–nitrogen bridges.[3d,12]



10

The π systems of $[W_3N_2Cl_{14}]^{2-}$ can be obtained in the same way and show the expected resemblance to that of the pentadienyl cation. **11** compares calculated W–N overlap populations, a measure of W–N bond orders, with C–C overlap populations in $C_5H_7^+$. The pattern of overlap populations for both molecules mirrors the pattern of bond lengths in **3** and **7**, **8**. Note the outer bonds are indicated as being stronger even though they enter the calculations "unprejudiced", with equal bond lengths. IR and Raman spectral data are also available for Os and Ru trimers such as $Os_3N_2(O)_2(OH)_7(NH_2)(NH_3)_4$ and $[Os_3N_2(NH_3)_8(OH_2)_6]Cl_6$ with d electron counts ranging from six to twelve. Some are asymmetrical; some are reported to be symmetrical.[13] Although we cannot predict the precise electron count at which all M–N bond lengths should become equal, the M–N π^* levels will begin being filled only after all five M–N nonbonding levels are occupied, at d electron counts greater than ten. Similar reasoning allows structural predictions for the higher oligomers and provides a rationale for the structures of the polymers analogous to polyacetylene.

11



Figures 1 and 2 illustrate the consequences of half-filling the nonbonding bands of a homomorphic and a heteromorphic polymeric π system. The reader is referred to several recent references for the requisite language of solid-state physics that we need to use here.[14] In Figure 1, a and b, schematic drawings of trans polyacetylene π bands are shown. The bands are plotted for two atoms per unit cell so that the original Brillouin zone has been halved. The degenerate nonbonding levels of the undistorted polymer appear at the zone boundary in Figure 1a (at $k = \pi/2a$ of the original Brillouin zone, where $\cos(\vec{k}\cdot\vec{R}) = 0$ and $\epsilon_j = \alpha_c$). One orbital is bonding within the unit cell and antibonding outside; the other is antibonding inside the cell and bonding outside. The pairing distortion shown in Figure 1b splits the degenerate levels, lowering the occupied, bonding band and stabilizing the distorted structure.

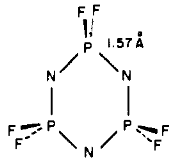
The π bands of the heteromorphic transition-metal nitride chain [Figure 2a,b] differ from the polyacetylene π bands in two important respects. First, orbital energies for this chain of alternating p and d orbitals depend on $\sin(\vec{k}\cdot\vec{R})$ so that the nonbonding levels of $\frac{1}{\infty}[Cl_4MoN^-]$ appear at the zone center, $k = 0$. Second, the nonbonding levels are concentrated on alternate atoms with $\alpha_M \neq \alpha_N$ so the nonbonding levels are nondegenerate even in the symmetric, nonalternating structure. A pairing distortion similar to the Peierls distortion in polyacetylene can nevertheless occur (Figure 2b). The driving force for the distortion, when it does occur, is a second-order mixing of the nonbonding orbitals. The extent of this second-order Jahn–Teller distortion can be controlled by tuning the HOMO–LUMO gap.[2,15]

In addition to the allyl, pentadienyl, and polyacetylene analogues we fully expect the synthesis of other finite $(ML_n)_xN_y$ oligomers.

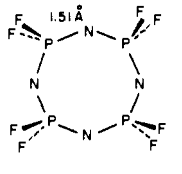
The reader who is sensitive to the history of theoretical chemistry will have long ago grown impatient with our failure to introduce the obviously related phosphonitrilic halides or phosphazenes into the discussion. We have procrastinated not out of ignorance of these beautiful molecules[16] but because their relationship enters most naturally in discussing the tetramer.

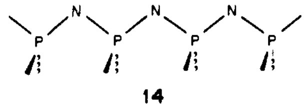
The phosphazenes are oligomers of X_2PN (X = halogen, R, etc.). The most common representatives are trimers, **12**, tetramers, **13**, and the polymer, **14**.

12



13





14

Phosphorus–nitrogen bond lengths in the cyclic phosphazenes contrast sharply with the bond length alternation found for polyenes and transition-metal nitrides. Approximately planar six- *and* eight-membered rings have all P–N distances equal. Bond lengths, shown in **12** and **13**, are significantly shorter than the P–N single bond distance of ~1.78 Å. Some of the symmetrically

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(12) (a) Weller, F.; Liebelt, W.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1982**, *484*, 124. (b) Weller, F.; Liebelt, W.; Dehnicke, K. *Angew. Chem.* **1980**, *92*, 211. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 220.

(13) (a) Hall, J. P.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* **1980**, 2410. (b) Griffith, W. P.; Pawson, D. *J. Chem. Soc., Dalton Trans.* **1973**, 1315. (c) Cleare, M. J.; Griffith, W. P. *J. Chem. Soc. A* **1970**, 1117. (d) Watt, G. W.; McMordie, W. C., Jr. *J. Inorg. Nucl. Chem.* **1965**, *27*, 2013.

(14) (a) Burdett, J. K. *Prog. Solid State Chem.* **1984**, *15*, 173. (b) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; Wiley-Interscience: New York, 1985; Chapter 20. (c) Ashcroft, N. W.; Mermin, N. D. *Solid State Physics*; Holt, Rhinehart, and Winston: New York, 1976; Chapters 8–10.

(15) Lowe, J. P.; Kafafi, S. A. *J. Am. Chem. Soc.* **1984**, *106*, 5837.

(16) For reviews of cyclic phosphazenes and related compounds, see: (a) Heal, H. G. *The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus*; Academic Press: London, 1980; Chapter 12 and references therein. (b) Krishnamurthy, S. S.; Sau, A. C.; Woods, M. *Adv. Inorg. Chem. Radiochem.* **1978**, *21*, 41. (c) Allcock, H. R. *Chem. Rev.* **1972**, *72*, 315. (d) Allcock, H. R. *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972. (e) Allcock, H. R. *Heteroatom Ring System and Polymers*; Academic Press: New York, 1967. (f) For a recent calculation on $(H_2PN)_{2,3}$ see: Trinquier, G. *J. Am. Chem. Soc.* **1986**, *108*, 568.

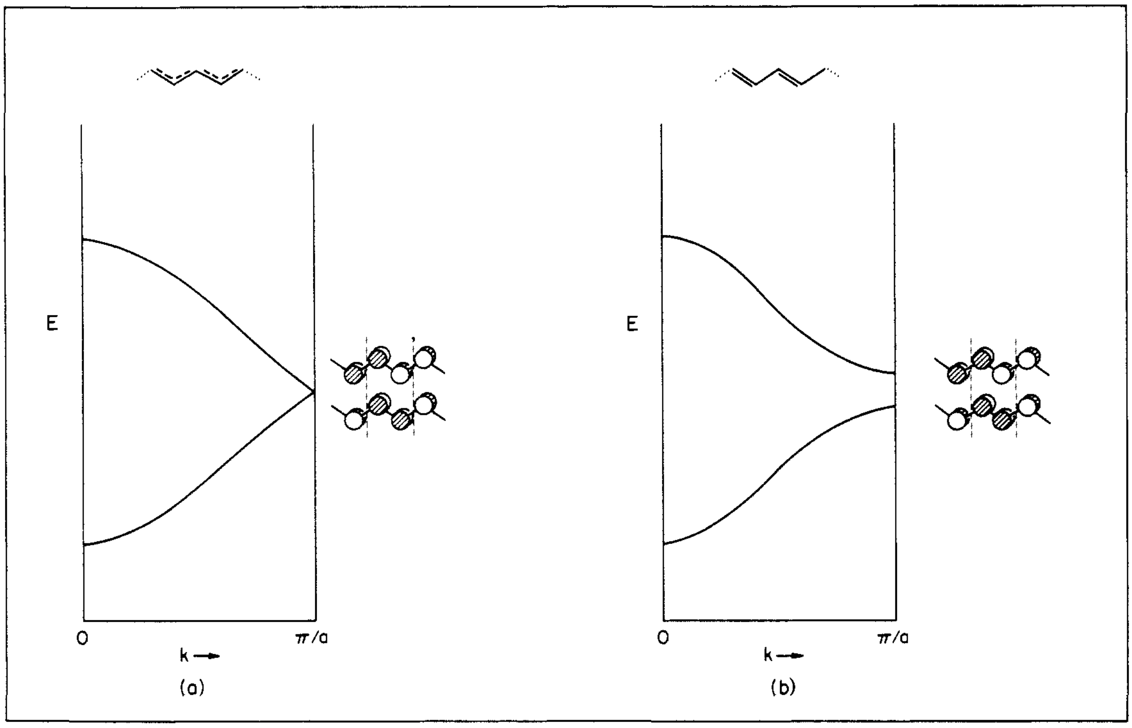
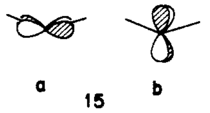


Figure 1. Schematic π bands of trans polyacetylene showing the effect of introducing bond alternation. Bands are plotted for two carbon atoms in the unit cell so the original Brillouin zone has been halved.

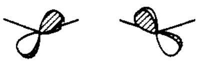
substituted tetramers adopt significantly nonplanar geometries but do not show bond alternation.

The apparent benzenoid stability of the phosphonitrilic halides set the stage 25 years ago for an instructive polemic concerning their electronic structure. Let us try to summarize here the discussion of Craig and Paddock[17] and Dewar[18] and its relation to the transition-metal nitride problem.

Assuming the σ bonds form from sp^3 hybrids on phosphorus, Craig suggested that participation of the tangentially directed, heteromorphic d_π orbitals shown in **15a** should lead to cyclic delocalization of the π electrons in $(NPCl_2)_3$. Dewar et al. recognized that a Hückel treatment including radial d orbitals of the type **15b** (with $\alpha_{rad} = \alpha_{tang}$) results in delocalization only over allylic P–N–P units. The two d orbitals at one P can be chosen as the equivalent orthogonal pair **16**. Each then participates in an independent three-center two-electron bonding system, one of which is drawn in **17**.

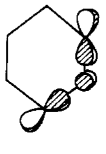


a **15** b



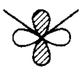
a **16** b

17



The two models predicted different stabilities with increasing ring size. Craig's heteromorphic π system has a Hückel topology for an even number of P atoms and a Möbius topology[19] for an odd number. The delocalization energy per ring atom increases with ring size, but then it is never greater than the delocalization energy in antiaromatic systems such as cyclobutadiene or planar cyclooctatetraene. Dewar, viewing the phosphonitrilic halides as a totality of three-center islands, unconjugated at their ends, would say these compounds are nonaromatic.

Craig and Paddock have also noted that in-plane π orbitals of the type shown in **18** are probably unimportant in the phosphazenes.[20] We find that it is precisely these homomorphic, in-plane π orbitals that determine metal–nitrogen bond lengths in the cyclic transition-metal nitrides.



18

The π bonding orbitals of D_{4h} $[Cl_4MoN^-]_4$, shown on the left of Figure 3, show features of both the Dewar and the Craig models of phosphazene π bonding. The out-of-plane π orbitals form a degenerate pair of allylic type orbitals as well as two completely bonding combinations of nitrogen p_z with radial and tangential metal d orbitals. The in-plane π orbitals (with Hückel energies $\epsilon_j = [(\alpha_M + \alpha_N) \pm ((\alpha_M - \alpha_N) + 16\,\beta^2 \cos^2 (2\pi j/N))^{1/2}]/2)$ have a nodal pattern reminiscent of planar cyclooctatetraene. A totally bonding MO is located below a degenerate pair of π bonding orbitals having a single node. The nonbonding orbitals are noded on Mo or on N just as the nonbonding orbitals of C_8H_8 have nodes on alternate carbon atoms. In both $[Cl_4MoN^-]_4$ and C_8H_8 the nonbonding orbitals contain a total of two electrons. But in the MoN tetramer these two nonbonding orbitals are not degenerate.

Nevertheless the tetramer distorts, even if it does not have a first-order Jahn–Teller reason for doing so. Figure 3 shows how distorting the molecule from one with equal Mo–N bond lengths (D_{4h} symmetry) to a molecule having alternating long and short bonds (C_{4h}) causes the HOMO and LUMO to mix. The lowest occupied nonbonding orbital gains Mo–N bonding character, drops in energy, and stabilizes the distorted structure. The other orbitals remain almost constant in energy and do not take part in the second-order Jahn–Teller distortion.

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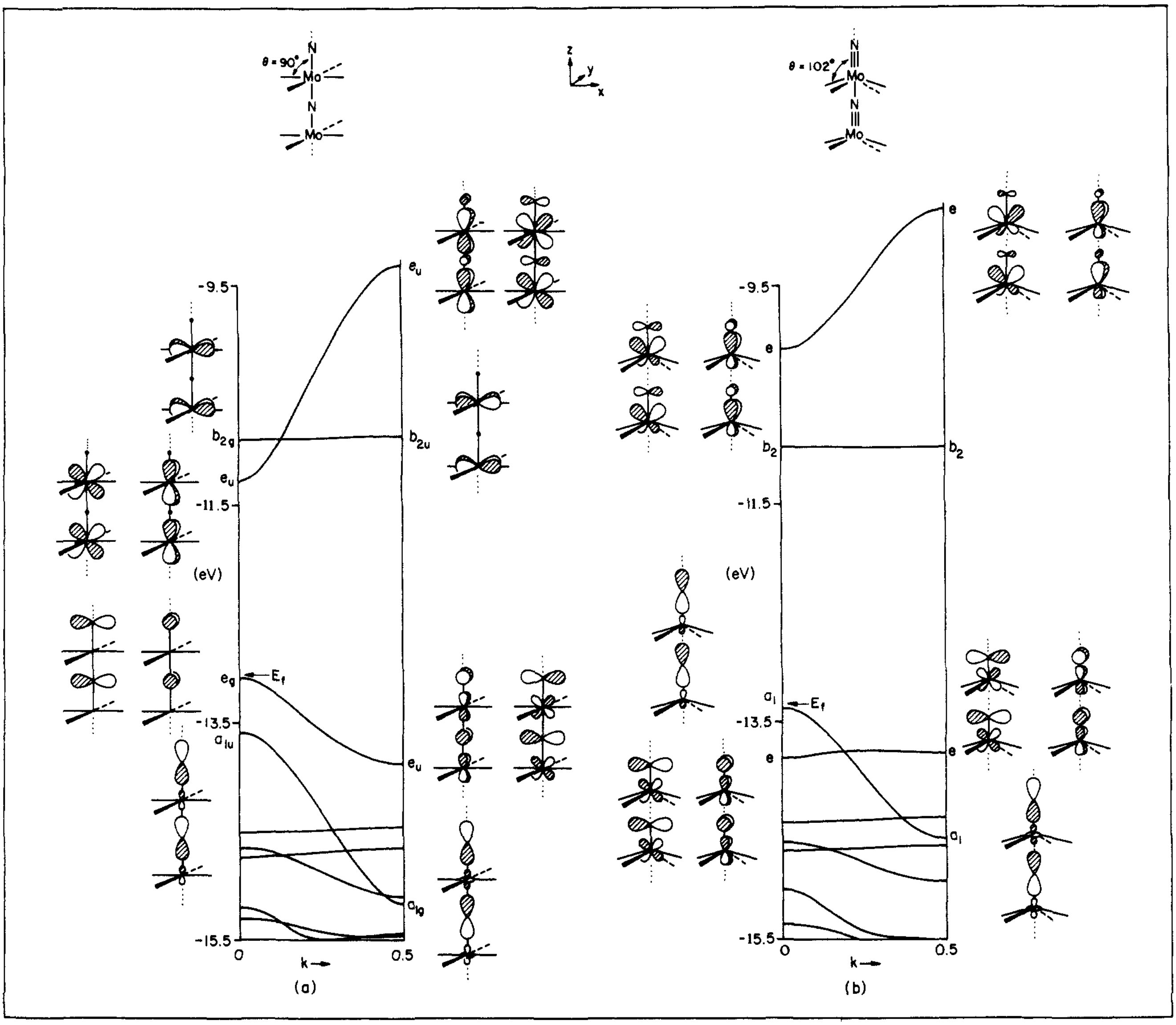
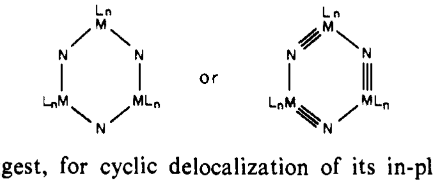


Figure 2. Band structures of polymeric $MoNCl_4^-$ showing HOMO-LUMO mixing at $k = 0$ when the point symmetry is lowered from D_{4h} (a) to C_{4v} (b) by introducing Mo-N bond length alternation and pyramidalizing about the metal.

Perhaps the most interesting conclusion we draw for the transition-metal nitrides is that there should be substantial stability for a benzene analogue. No such trimer, $(L_nMN)_3$, **19**, has been synthesized, as far as we know. It is a worthwhile synthetic target,

19



we would suggest, for cyclic delocalization of its in-plane π electrons should give it considerable stability.

Does this mean that the benzene analogue **19** will have all equal MN bond lengths? We are not sure. In polyenes even $4n + 2$, aromatic, Hückel systems have a point at which they localize, around $n = 4$.[8,21] Localization is likely to set in earlier the smaller the coupling overlap.[22] Extended Hückel calculations, which are unreliable for bond lengths, appear to favor localization, while stabilization, as defined by a resonance energy, is retained.

The observed bonding patterns for dimeric cyclobutadiene analogues are complicated. Nitrido-bridged *dimers* such as $[X_4MoN^-]_2$ are unknown, but oxo[23a,b] and halide[23c] bridged dimers generally have equal bond lengths within the planar ring.[23d] Various distortions in these molecules have been considered previously.[24] Alkylidyne, alkoxide, and imide bridged dimers showing bond alternation have been isolated,[25] and bond lengths in the imide compounds have been discussed in terms of the aromatic or antiaromatic character of the out-of-plane π systems.[25e] The possibility of metal-metal bonding further com-

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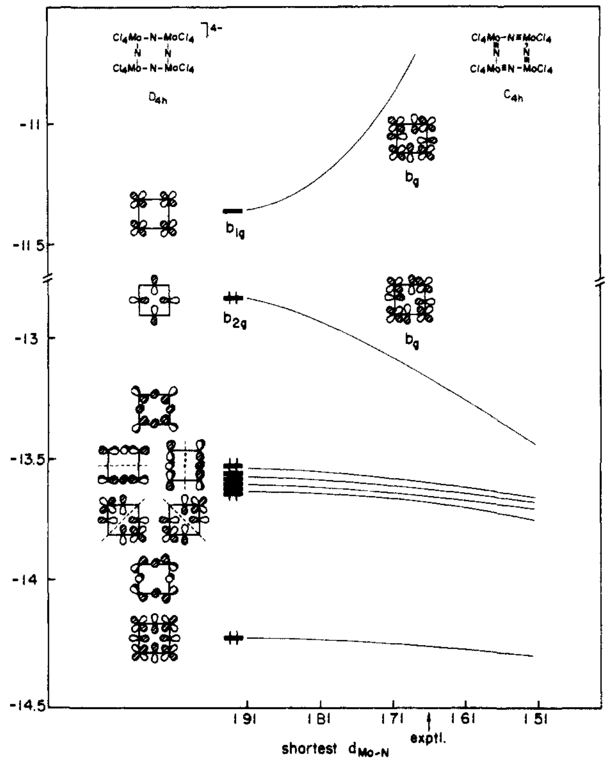
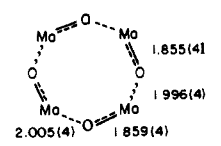


Figure 3. Correlation diagram showing the mixing of Mo-based b_{1g} and N-localized b_{2g} in the second-order Jahn–Teller distortion which drives Mo–N bond length alternation.

plicates the situation in the smaller rings.[24b,26]

Before leaving the $(L_nMN)_x$ cyclic systems we might note that bond alternation reminiscent of what we see so clearly in the tetramer occurs also in polycyclic, cluster structures of the polymolybdate or tungstate type. This was recently pointed out by Klemperer, Day, and co-workers and by Fuchs et al.[27b] A typical example is **20**, an eight-membered ring extracted from a $Mo_6O_{19}^{2-}$ structure.[28] The alternation is much more attenuated than in the nitride tetramers, but it is likely to have similar origins.

20



We have analyzed the alternation in the metal nitride tetramers and traced it to a second-order Jahn–Teller mixing. Now let us try to address the question as to why the corresponding tetrameric phosphazenes do not show the alternation.

The same π orbitals found for $[Cl_4MoN^-]_4$ exist in the symmetrical, tetrameric phosphazenes like $(NPF_2)_4$, but the effect of the in-plane π orbitals is greatly reduced. The relevant π orbitals of $(NPF_2)_4$ are shown in Figure 4. We will not discuss here the out-of-plane π orbitals, whose energies are marked in Figure 4, but focus on the in-plane π orbitals, which are drawn out. The counterparts to the frontier orbitals for $(L_n\mathit{MoN})_4$ are easily seen in Figure 4. They are filled b_{2g} (mostly on the N) and empty b_{1g}, mainly on P. Upon bond alternation these will mix, but their overlap is poorer and they are much further apart in energy. The driving force for deformation is very much reduced. Our calculations indicate that without 3d orbitals on phosphorus, $(F_2PN)_4$ is predicted to be symmetrical, which is the way it is.

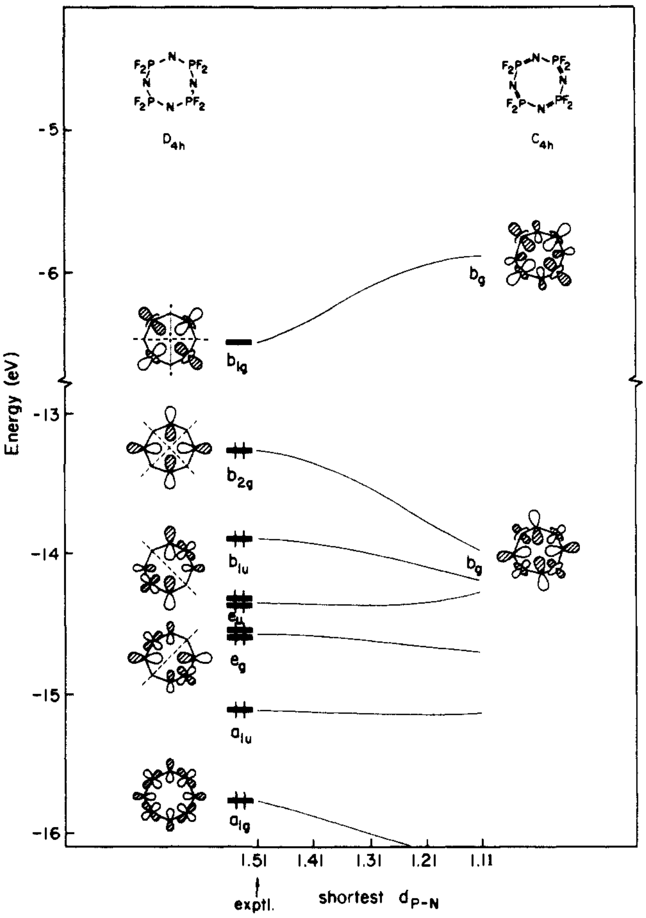


Figure 4. Correlation diagram showing the mixing of b_{1g}, located mainly on phosphorus, and b_{2g}, concentrated on nitrogen, upon bond length alternation. The π orbitals of $(F_2PN)_4$ are similar to those of $(L_n\mathit{MoN})_4$ (see Figure 3) except for the 7-eV HOMO–LUMO gap.

What about the d orbitals? A word is in place here about the general problem of the involvement of 3d orbitals in second-row chemistry.[29] There was a long period when d orbitals on Si, P, S, and Cl were used as a *deus ex machina* to rationalize any puzzling chemical or physical observation in compounds of these elements, especially in hypervalent bonding situations. It then became clear that in many cases the d orbitals were not essential, but that PR_n σ^* orbitals could serve the same function by essentially a hyperconjugative mechanism.[30] The present balanced picture, as we see it, admits that d orbitals are there, that they may be involved in tailoring wave functions and so be energetically important,[31] but they are not inherently essential, that indeed PR_n σ^* orbitals may often play the necessary acceptor role, or some admixture of d and π^* orbitals.[32] It should also be said that the strategy for enhancing the role of second-row element d orbitals is clear—one needs to make the d functions more contracted for effective overlap and to bring them lower in energy. This is accomplished by substituting the element (here P) with electronegative groups to make it more positive and by providing a good adjacent π donor to enhance, symbiotically, its acceptor characteristics.

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Table II. Parameters Used in the Extended Hückel Calculations

orbital		H_{ii} (eV)	ζ_1	ζ_2	$C_1{}^a$	$C_2{}^a$
Mo	4d	−12.30	4.54	1.90	0.5899	0.5899
	5s	−9.66	1.956			
	5p	−6.36	1.90			
W	5d	−10.40	4.98	2.07	0.6683	0.5422
	6s	−8.62	2.34			
	6p	−5.17	2.31			
P	3d	−7	1.4			
	3s	−18.6	1.60			
	3p	−14.0	1.60			
N	2s	−26.0	1.95			
	2p	−13.4	1.95			
Cl	3s	−30.0	2.033			
	3p	−15.0	2.033			
F	2s	−40.0	2.425			
	2p	−18.1	2.425			

[a] Coefficients used in the double-ζ expansion of the d orbitals.

In the case at hand of cyclic P containing compounds some interactions (**15b**) can be played out equally well by PX_2 σ^* as by 3d on P. But others (**15a**, **18**) have no PX_2 σ^* symmetry equivalent. So P 3d orbitals could play a role, especially if the in-plane π system were important, as we concluded it is in $(L_nMoN)_4$. We repeated our calculations on $(F_2PN)_4$ with 3d orbitals on P, placed at various energies. In each case a localized, bond-alternating structure is computed. But the degree of alternation is much smaller than in the transition-metal nitride case. We do not want to say that this is an argument against the involvement of 3d orbitals. More likely it is a failure of the extended Hückel method, or insufficient geometry optimization. The many known molecules may pucker to varying degrees, but they retain (with some exceptions) equal P–N bond lengths. We would nevertheless keep an eye out for small bond alternation.

To summarize: (1) There is an obvious analogy between d–p π orbitals of linear and cyclic early transition-metal nitrides and the p π orbitals of polyenes. This leads to predicted stability for some as yet unsynthesized MoN oligomers such as the cyclic trimer. (2) There should be a continuum of delocalization and tendency to localize or alternate bonds in cyclic heteromorphic systems. The 4*n* systems will localize by a second-order Jahn–Teller mechanism when the energy splitting between the (nondegenerate) nonbonding orbital combinations is relatively small. It is so in the $(L_nMoN)_4$ system but not in $(X_2PN)_4$.

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Appendix

The Extended Hückel method was used for all calculations.[33] Parameters[34] are listed in Table II. Mo–N and Mo–Cl bond lengths were taken from the $[MoNCl_3{\cdot}O(C_4H_9)_2]_4$ X-ray structure.[35] Experimental bond lengths were also used for $[W_3N_2Cl_{14}]^{2-}$ [1c] and $(F_2PN)_4$.[36]

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The Contribution of π Electrons to Second Harmonic Generation in Organic Molecules

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Abstract: The frequency-dependent hyperpolarizability for sum frequency generation is calculated within a π electron approximation for a series of unsaturated organic compounds and compared to experimental data measured in polar and nonpolar liquid media. A procedure is also suggested to investigate the influence of electrostatic intermolecular interaction on the hyperpolarizability of small clusters of molecules in relative positions corresponding to the crystal structure.

I. Introduction

For about a decade an active and systematic search has been conducted for materials exhibiting large optical nonlinear responses. Much attention has been given to organic compounds, in view of their application to second harmonic generation (SHG) from the near infrared to the visible. It has been observed that particular, noncentrosymmetric polar unsaturated molecules may exhibit unusually large hyperpolarizabilities.[1-26] Molecules in which intramolecular charge-transfer transitions occur and in which the dipole moments of the excited states are large appear to be particularly suited for this purpose. Efficient SHG furthermore requires the doubled frequency still to lie in the region where the molecule is transparent; it should however not be too far removed from the lowest frequency transitions. There is every

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