at least an equally satisfactory *quantitative* fit of the data to that mechanism over the very wide ranges of [complex], [O_2], and [CO] used. This has still not been done.

All this is not to say, of course, that further testing of the validity of the homolytic fission mechanism is not required. More experiments designed specifically to show different results for the different possible mechanisms would clearly be important, but it would equally clearly be unwise at this stage to dismiss the homolytic fission mechanism out of hand.

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Bent's Rule: Energetics, Electronegativity, and the Structures of Nonmetal Fluorides

Sir:

Bent's rule,[1] "*atomic s character tends to concentrate in orbitals that are directed toward electropositive groups and atomic p character tends to concentrate in orbitals that are directed toward electronegative groups*", has proved to be useful in explaining many aspects of the structural chemistry of organic and inorganic compounds.[1,2a] Furthermore, it is often cited as good chemical "horse sense" in theoretical studies.[3] Despite its success in the simple rationalization of molecular structures, little discussion of the physical basis of the effect has appeared. Bent[1] suggested, on the basis of perturbation theory, that isovalent hybridization should occur to transfer more s character to the electropositive-bonding orbital, since that transfer would maximize the bonding energy: The electrons bonding the electropositive element would be lowered in energy more than those bonding the electronegative element would be raised.

Grim et al.[4] have reported an apparent exception to Bent's rule, and, on the basis of this and other considerations, the Rule was modified in terms of orbital energy matching and overlap: "*The p character tends to concentrate in orbitals with weak covalency (arising from either electronegativity or overlap considerations), and s character tends to concentrate in orbitals with strong covalency (matched electronegativities and good overlap)*".[2b] The present communication suggests an extension and amplification of this point of view that, although not conflicting with the views of previous workers, provides a simple rationale for the operation of Bent's rule in molecules with highly electronegative substituents, provides an explanation for the s affinity of lone pairs (LP) in terms of energetics and Bent's rule, and furthermore helps rationalize the structures of certain nonmetal fluorides.

Consider the series of phosphorus fluorides, XPF_3 (where X = LP, BH_3, S, etc.), their respective FPF bond angles, and the corresponding s character of the X- and F-directed orbitals on the phosphorus atom (P_X and P_F, respectively):

compd	FPF, deg	% s P_F	% s P_X
$:PF_3$	97.8[4]	11.9	64.1
H_3BPF_3	100[5]	15	55
SPF_3	100.3[6]	15.2	54.5
OPF_3	101.3[6]	16.4	50.8
PF_4^+	109.5	25.0	25.0

Gillespie[8] has suggested that a lone pair can be considered to be a "substituent" with an effective electronegativity of zero since the lone pair is under the complete control of a single nucleus. Thus the above series contains substituents on the $-PF_3$ moiety ranging in electronegativity from 0 to 4 (Pauling scale). The FPF bond angle (and the s character of the fluorine-bonding phosphorus orbitals, P_F) increases as the amount of s character devoted to the fourth substituent (LP, B, S, O, F) decreases, as expected for isovalent hybridization according to Bent's rule. Boron behaves as a somewhat *more* electronegative atom (FPF angle larger) than expected because of the formal positive charge that it induces on the phosphorus atom. On the other hand, the oxygen atom appears to be somewhat *less* electronegative (as interpreted from the bond angles) than expected because of the extra VSEPR effect of the O=P double bond (see below).[2c,8,9] Note that the formally isoelectronic, but non-double-bonded, ONF_3 has bond angles closely approaching those of a tetrahedral molecule.[9]

Consider the following limits for the s character in the fluorine-bonding phosphorus orbitals of the compounds listed above. At the covalent or high-s limit (PF_4^+), all of the orbitals are identical sp^3 (te) hybrid orbitals. The change from the ground state of the nonbonded phosphorus atom to that in the fluorophosphonium ion, PF_4^+, will be $3s^2\,3p^1\,3p^1\,3p^1 \rightarrow 3s^1\,3p^1\,3p^1\,3p^1 + e$. The ionic or low-s limit (X = lone pair) is for the wave function corresponding to the ionic contributing structure in the resonance

$$:PF_3 \leftrightarrow :P^{+3} + 3F^-$$

with a change from ground state to the valence state of $3s^2\,3p^1\,3p^1\,3p^1 \rightarrow 3s^2\,3p^0\,3p^0\,3p^0$. In this limit, it is energetically favorable to ionize the higher energy 3p electrons and allow the lone pair to consist solely of the lower energy 3s pair. A configuration $3s^1\,3p^1\,3p^0\,3p^0$ would represent an excited state and contribute little to the ionic structure above. The energies involved are thus closely related to those of unsymmetrical hybridization.[2d] While it might be argued that complete ionization of the 3p electrons is an unrealistic limit in a predominantly covalent molecule, the partial ionization potential–electron affinity energy of covalent molecules is an important component of total bonding energy.[1,11]

Some interesting consequences of the energies associated with Bent's rule are shown by various nonmetal fluorides. The appropriate application of Bent's rule in conjunction with the VSEPR rules of Gillespie[8,9] provides insight into the detailed structure of these molecules. In the following discussion, the *z* axis is taken as the rotational axis of highest order in the trigonal bipyramid and square pyramid, the *x* axis as the second axis lying in the plane of the paper, and the *y* axis as the axis perpendicular to the paper. In accordance with common usage, axial substituents shall be those lying along the *z* axis, and equatorial substituents shall be those lying in the *xy* plane.

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0020-1669/81/1320-4033$01.25/0

Consider first the square pyramidal molecules ClF_5 and BrF_5. The axial X–F bond trans to the lone pair is shorter and stronger than the four equatorial bonds cis to the lone pair.[12] In addition, the lone pair should, on the basis of Bent's rule, attract more s character than the electronegative fluorine atoms. However, the five fluorine atoms will not attract p character equally even though they are presumably of the same inherent electronegativity. As we have seen from electronegativity arguments[2b,4] and a consideration of energetics (above), the *difference in electronegativity* between the central atom and the fluorine atom(s) appears to be responsible for the effects of Bent's rule. In XF_5 molecules, the central halogen atom is anisotropic with regard to electronegativity from the viewpoint of either hybridization (VBT) or a four-electron-three-center bond (MOT).

In terms of hybridization, the central atom may be considered to bond through a set of six quasi-sp digonal hybrids (ϕ_x, ϕ_{-x}, ϕ_y, ϕ_{-y}, ϕ_z, ϕ_{-z}) of the form[13]

$$\phi_x = (1/3)^{-1/2}\psi_s + \psi_{p_x} \qquad \phi_{-x} = (1/3)^{-1/2}\psi_s - \psi_{p_x}, \text{ etc.}$$

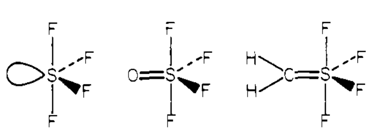
The four fluorine atoms cis to the lone pair will bond through four identical quasi-sp digonal hybrid orbitals. However, because of attraction of s character to the lone pair, the LP hybrid will be enriched in s character at the expense of the hybrid orbital trans to the lone pair, which is depleted in s character: For the ϕ_x and ϕ_{-x} orbitals the weighting coefficients will no longer be $(1/6)^{-1/2}$ and 1. The loss of s character will reduce the overlap of the axial orbital, but in bonds as polar as these, that does not appear to be a critical factor. Much more important is that since the electronegativity of an s–p hybrid orbital is directly proportional to the s character,[14] the central halogen atom will appear less electronegative toward the axial fluorine atom. Thus, on the basis of Pauling's ionic resonance energy[15] and the Schomaker–Stevenson equation,[16] the axial, trans X–F bond should be stronger and shorter than the four equatorial bonds cis to the lone pair.

In comparison, from the molecular orbital viewpoint, the four-electron three-center bonds should involve orbitals depleted of electrons (more electronegative) from the action of two electron-withdrawing fluorine atoms, whereas the trans orbital is less electronegative as a result of the action of a single fluorine atom and the polarizable, electron-donating lone pair. This line of reasoning is similar to that of Christe[12] in formulating a set of rules similar to that of Bent.

Other interesting molecules have recently been discussed by Christe and Oberhammer.[9] They have cogently argued, on the basis of bond angles in some other nonmetal fluorides, for directional VSEPR effects from π bonds. Although the two methods are in general agreement, the repulsive effects arising from Pauli forces in VSEPR do not *necessarily* correlate with the hybridization energetics implicit in Bent's rule. To the extent that they *do* agree, "prediction" is simplified; when they differ, "prediction" may be confounded but "explanation" clarified.

A simple example of the difference in approach between the two ways of viewing molecular structure may be found in molecules discussed by Christe and Oberhammer: The FPF angle is 97.8° in PF_3 but 101.2° in OPF_3. This may be taken as greater repulsion by the lone pair in PF_3 than by the multiple-bonded oxygen in OPF_3[9] or as the tendency of a nonbonding electron pair to attract s character.[1,11] The "truth" probably lies somewhere between. The definitive test is given by Christe and Oberhammer:[9] In $OXeF_4$, the repulsion from the oxygen atom is greater than that of the lone pair trans to it, and the equatorial fluorine atoms are displaced away from the oxygen with OXeF angle = 91.8°. A similar comparison, OIF_5 vs. IF_5, though in the same direction, is hardly convincing since the bond angles are almost identical (98.0°, 97.9°).

Chart I



Axial FSF angle (idealized = 180°)	173°	164°	170°
Equatorial FSF angle (idealized = 120°)	101°	115°	97°

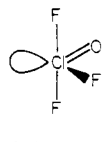
In contrast to the clear-cut, VSEPR-effects-only case of $OXeF_4$, the Christe–Oberhammer series XSF_4 with X = LP, O, and CH_2 illustrates complementary and competing forces (see Chart I). In SF_4, the axial FSF angle is compressed moderately ($\Delta = -7°$) from VSEPR effects from the lone pair. Viewed from VSEPR effects alone, the greater compression of the equatorial FSF angle ($\Delta = -19°$) is surprising, since 90° interactions (lone pair–axial fluorine) are more intense than 120° interactions (lone pair–equatorial fluorine)[2e]. The decrease in FSF_{eq} angle results in part from the added effect of Bent's rule: The lone pair attracts s character, leaving more p character and a smaller bond angle for the fluorine atoms.

In OSF_4, the axial FSF angle ($\Delta = -16°$) indicates greater VSEPR effects (in this case strongly directional[9]). However, the equatorial FSF angle *opens* to 115° ($\Delta = -5°$) compared to that in SF_4 confirming that the small value of the latter angle results from effects *in addition* to VSEPR. The greater electronegativity of oxygen makes the three equatorial substituents comparable and the deviations from ideality small.

The molecule CH_2SF_4 is of interest for several reasons. First, since the methylenic hydrogen atoms lie in the axial FSF plane rather than in the sterically more relaxed equatorial FSF plane, the general principle that *intra*atomic (VSEPR) Pauli repulsions are more important in molecules of interest to the inorganic chemist than are the *inter*atomic (van der Waals) Pauli repulsions[2f] is strengthened. The VSEPR-active π electrons of the C=S bond could lie in the *xz* plane ($\pi = p_z + d_{xz}$) or the *xy* plane ($\pi = p_y + d_{xy}$); their preference for the *xy* plane is indicative that the π pair–equatorial bonding pair interaction is energetically more favorable than the hydrogen atom–axial fluorine atom interaction is unfavorable. As a result of the orientation of the methylene group, the VSEPR effects are less pronounced axially ($\Delta = -10°$) than equatorially ($\Delta = -23°$). This, coupled with the low electronegativity of the methylene group (not so low as that of a lone pair, but directionally more important), results in a combined VSEPR *plus* Bent's rule effect restricting the FSF_{eq} angle to 97°.

A reviewer (see also ref 2g) has suggested that if CH_2SF_4 is viewed with a bent C=S double bond, the use of octahedral d^2sp^3 hybrid orbitals gives the correct geometry. This is yet another example of the high degree of "VSEPR horse sense" that was built into the commonly formulated hybrid orbitals.

Finally, in $OClF_3$, Bent's rule is responsible for the closing of the



OClF bond angle to 108.9° ($\Delta = -11.1°$), which would hardly

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[12] K. O. Christe, *Plenary Main Sect. Lect. Int. Congr. Pure Appl. Chem., 24th*, **4**, 115 (1974).

[13] The addition of $\psi_{d_{x^2-y^2}}$ and $\psi_{d_{z^2}}$ to form conventional $d^2\,sp^3$ hybrids does not change the argument here.

[14] H. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, **84**, 540 (1962); J. Hinze, M. A. Whitehead, and H. H. Jaffé, *ibid.*, **85**, 148 (1963).

[15] L. Pauling, "The Nature of the Chemical Bond", 3rd ed., Cornell University Press, Ithaca, N.Y., 1960.

[16] V. Schomaker and D. P. Stevenson, *J. Am. Chem. Soc.*, **63**, 37 (1941).

have been expected on the basis of VSEPR alone since, even considering the directional character of the π-bonding electrons in the Cl=O double bond,[9] the oxygen should better be able to compete with the lone pair for equatorial space about the chlorine atom. Rather, the OClF angle closes down from a Bent's rule effect just as the FSF angle in SF_4 does. *However*, in $OClF_3$ the difference in electronegativity between the central chlorine atom and the substituent oxygen and fluorine atoms is considerably less (Δ_χ = ca. 0.6) than that between the central sulfur atom and the substituent fluorine atoms ($\Delta_\chi = 1.4$); therefore the angle trans to the lone pair closes only to 108.9° rather than to 101°. In contrast, the opening of the OClF angle to 94.7° (expected = 90°) *contrary* to Bent's rule is conclusive proof of the directional nature of the π interaction espoused by Christe and Oberhammer.

In summary, for isovalent hybridization of X–Y–Z systems, the more closely the electronegativities of X and Z match, the more important will be the covalent contribution to *both* bonds and the more nearly equal will be the s character of the two hybrid orbitals on atom Y. For Z much more electronegative than X, s character will tend to reside in the X-directed orbital and the easily ionized p character will be directed to the more highly ionic X-Z bond. Furthermore, differences in electronegativity between the central atom and the peripheral atoms are probably more important than the absolute electronegativity of the latter.

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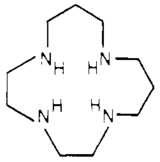
Coordination Behavior of the Tetraaza Macrocycle Isocyclam

Sir:

In a paper from this laboratory,[1] the synthesis of the 14-membered saturated tetraaza macrocycle isocyclam (1,4,7,11-tetraazacyclotetradecane (I)) as well as its coordinative behavior against the nickel(II) ion was described. Compounds containing both low-spin square-planar and high-spin pseudooctahedral nickel(II) chromophores were isolated, and both four- and six-coordinate species were found to coexist in aqueous solution according to a temperature-dependent equilibrium. For all of these nickel(II)–isocyclam moieties it was suggested that the ligand was planarly arranged around the metal ion, thus behaving as tetradentate.



I

More recently further work has been reported on the same subject by Blinn and co-workers.[2] They claim that in the square-planar nickel(II) derivatives only three nitrogen donors are bound to the metal ion with the uncoordinated fourth one potentially behaving as a Brønsted base in aqueous solution. This hypothesis is surprising for several reasons: (i) the stabilization of the singlet ground state of nickel(II) ion, in absence of steric effects,[3] is usually achieved through the coordination of four amine nitrogen donors; (ii) the exothermic heat of complex formation of metal ion–polyamine systems reflects the exothermic formation of metal–nitrogen coordination bonds,[4] and calorimetric investigations performed in this laboratory have recently shown[5] that the formation of the low-spin $[Ni(isocyclam)]^{2+}$ species is remarkably more exothermic than that of the homologous species with the corresponding 13-membered macrocycle. X-ray diffractometric studies have shown that in the latter compound the ligand acts as tetradentate.[6] Also, the formation of the nickel(II) complex with the isocyclam ligand is also more exothermic than that with the open-chain tetraamine trien, which surely acts as tetradentate.[7]

All of the above considerations strongly suggest that the isocyclam is fully coordinated to the metal ion in the low-spin complex, and we feel that Blinn and co-workers hypothesis on the tridentate behavior of the isocyclam is based on questionable experimental data. For example, they speculate on the increase of the pH value which they found to follow the dissolution in water of some solid complexes (but with no figures reported). Since the acidic or basic character of chemical species in aqueous solution can be clearly evidenced through a pH titration, we have performed the following experiments: two 10^{-2} M solutions of hydrochloric acid, one containing an equimolar amount of $Ni(isocyclam)(ClO_4)_2$, were potentiometrically titrated with a standard base. Two superimposable titration curves were obtained, without any inflection which would indicate the existence of some acid–base equilibria involving the macrocyclic moiety. It is well-known that, when a relatively pure material is dissolved in water, a pH change may occur as a consequence of the presence of basic or acidic impurities. It seems likely that this is the source of Blinn's pH effect.

Furthermore, Blinn and co-workers also investigated the octahedral–square-planar equilibrium which occurs, as mentioned above, in aqueous solution (eq 1). They confirm the

$$[Ni(isocyclam)(H_2O)_2]^{2+} \rightleftharpoons [Ni(isocyclam)]^{2+} + 2H_2O \qquad (1)$$

findings and thermodynamic quantities previously obtained in our laboratory. If in the low-spin complex one nitrogen donor were free and behaved as a base, as they proposed, addition of acid would displace equilibrium 1 to the right, favoring the formation of the low-spin species. A neutral aqueous solution of $Ni(isocyclam)(ClO_4)_2$ containing 60% of the low-spin species, as monitored by the intensity of the band at 463 nm, was spectrophotometrically titrated with standard acid. It was found that the progressive decrease of the pH (down to 2) did not involve any increase or decrease of the low-spin species.

Further information on the nature of the chromophores involved in equilibrium 1 is provided by the ^1H NMR of D_2O solutions of nickel(II)–isocyclam derivatives. The NMR traces consist of ten resonances, eight located downfield and two upfield as referenced to DSS standard. With the existence of equilibrium 1, involving both diamagnetic and paramagnetic chromophores, the observed pattern of resonances is very similar to that found for $CDCl_3$ solutions containing the fully paramagnetic $Ni(isocyclam)Cl_2$ complex[8] and unambiguously

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