$$M_\beta = \sum_{i=1,2,\ldots}{}' \langle \Phi_0(n)\Phi_\beta(n \pm i) \times |\mathrm{V}(n,n \pm i)| \Phi_\beta(n)\Phi_0(n \pm i)\rangle \quad (13)$$

is the energy shift due to various neighbor exciton interactions. In the case of (Chl a$\cdot H_2O)_2$, eq 13 may be explicitly rewritten in the point–dipole approximation[9]

$$M_\beta = \frac{e\mu^2}{R_{12}{}^3}\left[1 - \left(\frac{3R_\perp{}^2}{R_{12}{}^2} - 1\right)\sin^2\frac{\theta}{2}\right] \quad (14)$$

where μ, $R_\perp$, R_{12}, and θ are the monomeric transition dipole moment, the perpendicular distance between the two chlorin planes, the distance between, and the angle subtended by the transition dipoles, respectively.

The energies ϵ_0 and ϵ_β include all solvent interactions between the molecules and the surrounding medium. The difference between eq 11 and eq 4

$$\Delta E = \Delta\epsilon_{\beta 0} + \Delta\delta_{\beta 0} + M_\beta \cos(k_\nu a) \quad (15)$$

yields the energy gap between the ground state and the k_νth exciton component of the βth excited level. In eq 15 $\Delta\epsilon_{\beta 0} = \epsilon_\beta - \epsilon_0$ corresponds to the transition energy gap of the monomeric unit. The $\Delta\delta_{\beta 0} = \delta_\beta - \delta_0$ term signifies the difference between the aggregation energy of the excited state β and that of the ground state due to the change in *permanent* dipole moment in the excited molecule. For Chl a (and all polar molecules) the leading terms in eq 5 and eq 12 are of dipole-dipole origin.[22] For $(\mu_\beta - \mu_0) > 0$, we have $\Delta\delta_{\beta 0} < 0$ and a corresponding red shift in the aggregate absorption is obtained.

In a systematic analysis of exciton effects,[9] we find that $\Delta\delta_{\beta 0}$ is primarily responsible for the observed Chl a aggregation red shifts. The peak positions of monomeric hydrated Chl a, (Chl a$\cdot 2H_2O)_2$, (Chl a$\cdot H_2O)_2$, and (Chl a$\cdot 2H_2O)_n$ are respectively given 665 nm[3,9b] (A665), 695 nm[9b] (A695), 700 nm,[3,9b] and 743 nm[3,4] (A743) in 1:1 *n*-pentane:methylcyclohexane.[23] Assuming the red shift between A665 and A695, $\Delta\nu_{A695} = -649\ \mathrm{cm}^{-1}$, to be a unit of nearest neighbor dipole–dipole shift difference in (Chl a$\cdot 2H_2O)_n$, the frequency shift for A743 can be computed according to the formula

$$\Delta\nu_{A743} = \Delta\delta_{S_1 - S_0}(A743) = \sum_{i,1,2,\ldots} \frac{2\Delta\nu_{A695}}{i^3} = -1559\ \mathrm{cm}^{-1} \quad (16)$$

which gives 742 nm for the expected red-shifted (with respect to A665) absorption maximum position for (Chl a$\cdot 2H_2O)_n$, in excellent agreement with experiment. In eq 16 the summation over i converges rapidly in view of the cube dependence on the separation distance in dipole–dipole interaction. The factor of 2 in eq 16 reflects the translation symmetry in (Chl a$\cdot 2H_2O)_n$ as represented in Figure 6 of ref 15. The mth excited monomeric unit in (Chl a$\cdot 2H_2O)_n$ sees pairs of identical interactions with units at $m \pm 1$, $m \pm 2$, $m \pm 3$, ...

We attribute the relatively large red shift in hydrated Chl a aggregates compared to that in Chl a_2 to hydrogen bonding of the water proton to a Chl a carbonyl. The presence of the proton enhances the excited-state electronic redistribution in favor of the electronegative end of the C═O bond. The close proximity of the peak positions in (Chl a$\cdot H_2O)_2$ and (pyroChl$\cdot H_2O)_2$[9,10] suggests that the same effect may be operative when either of the two ring V carbonyl groups is involved. Current frequency shift studies in this laboratory are concerned with the effect of π-conjugation involving the chlorin macrocycle and with the consequences of geometrical differences in the proposed structures for (Chl a$\cdot H_2O)_2$ and (pyroChl$\cdot H_2O$), as well as the inclusion of the relatively minor frequency shift due to exciton interaction in eq 13.

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Tricoordinate Hypervalent Sulfur Compounds

Sir:

Molecular multicenter bonding which occurs when a given atom has more bonds than atomic orbitals as defined by the octet rule is termed hypervalent, and many examples are found

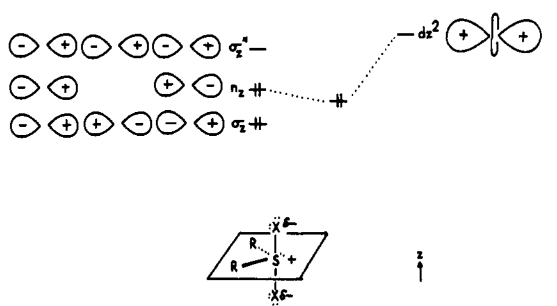


Figure 1. Axial bonding system in tetracovalent sulfuranes.

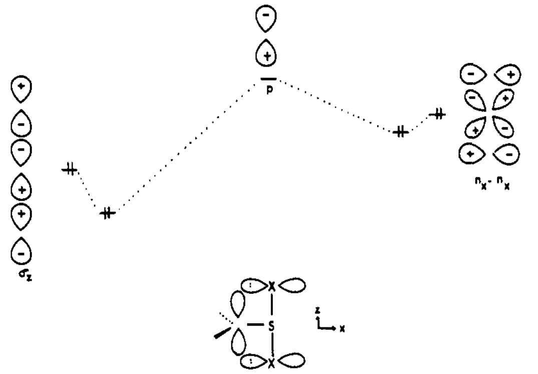


Figure 2. Axial interaction diagram for a parallel acceptor orbital.

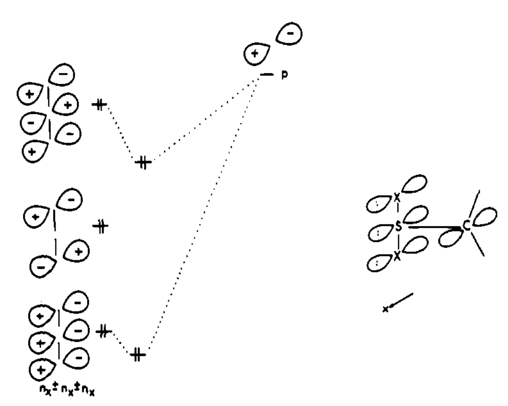


Figure 3. Axial interaction diagram for an orthogonal acceptor orbital.

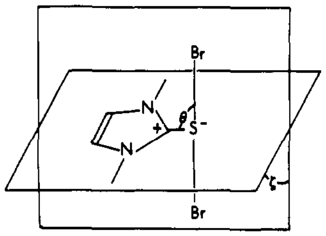
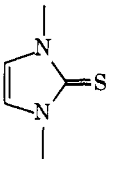


Figure 4. Solid state geometry of sulfurane **3a**.

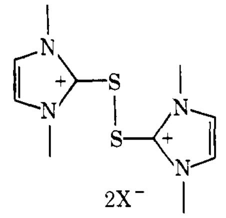
among the second- and third-row main-group elements. Aside from an enormous amount of theoretical interest[1] in such "orbitally deficient" molecules they also have found increasing importance as synthetic organic reagents and especially noteworthy in this latter regard is the work of Martin et al.[2] on tetracoordinate tetracovalent sulfurances. We now wish to report on a new class of hypervalent sulfur molecules, which are tricoordinate and tricovalent and have unique stability as compared to their tetracovalent counterparts.

The trigonal bipyramidal geometry, observed[3] for tetracovalent sulfuranes, is a result of the enforced 3-center linear axial (z) orbitally deficient bonding arrangement whose orbitals are simplified in Figure 1. In such molecules electrons are required to fill high-lying nonbonding orbitals (n_z) ccntered on the apical ligands (X). This leads to bonding only from the 2-electron 3-center orbital array σ_z while the balance of the axial electron density must be delocalized away from the central atom toward the ligands and thus stabilization is achieved by increasing electronegative apical groups. The effect of higher order (for S, 3d or 4s) orbitals on the central atom in the basis set on the calculated Hartree-Fock energy seems to be minimal.[1] Use of these more diffuse orbitals which have the proper symmetry to mix with n_z (i.e., d_{z^2} in Figure 1) seems to serve only the purpose of an improved basis set allowing a small shift in electron density from ligand to the central atom. Hypervalent sulfur molecules would experience a stabilizing total energy decrease if ligand electron density could be delocalized to a equatorial substituent and this could be accomplished by the placement of a low-lying π-acceptor substituent orbital of proper symmetry centered in the equatorial plane. The two possible orientations of this acceptor orbital with the axial XSX bonding system are parallel and orthogonal. The symmetry for interaction of a parallel π-acceptor (p) with the axial σ_z orbital and the ligand nonbonding orbital ($n_z - n_z$), is shown in Figure 2. Rotation allows interaction of the π-acceptor with the axial ligand central atom nonbonding levels ($n_x + n_x + n_x$) and ($n_x - n_x + n_x$) with the resultant stabilization as shown in Figure 3. We must conclude that the latter alignment is favored and calculate the total energy difference to be ~12 kcal/mol for a hypothetical geometry-optimized tricoordinate sulfurane, H_2CSCl_2.[4] The energetic placement of the low-lying-acceptor orbital is critical and the 6π-electron aromatic imidazolium cation appeared to be a suitable synthetic candidate for this substituent.

Reaction of 1,3-dimethylimidazolthione[5] (**1**) with 0.5 equiv of bromine at 0 °C in CH_2Cl_2 solution gives the disulfide **2a**,[6] mp 240–241 °C dec. Further bromination of **2a** under the same conditions affords in high yield the stable tricoordinate tricovalent sulfurane **3a**, mp 173–174 °C dec. A single crystal of



1



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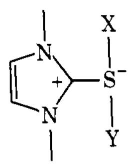

3

a, X = Y = Br
b, X = Y = Cl
c, X = Br; Y = I

3a was analyzed by x-ray diffraction: monoclinic; $a = 8.018$, $b = 14.396$, $c = 16.403$ Å; $\beta = 95.53°$, $V = 1893$ Å^3; $Z = 8$, $\rho_{\text{calcd}} = 2.029$ g/cm^3; space group $P2_1/C$ from systematic absences, $h0l$, when $l = 2n + 1$, $0k0$, when $k = 2n + 1$, Mo Kα X-radiation at a takeoff angle of 6.5 using a SYNTEX $P2_1$ diffractometer. A total of 3254 nonzero reflections were refined to a crystallographic R factor of 0.062, and the resultant structure is shown in Figure 4.

In complete agreement with the theoretically derived geometry this sulfurane has an axial 3-center geometry almost collinear ($\theta = 87. \pm 0.8$) with elongated bonds of 2.520 and 2.477 ± 0.077) Å (cf. 2.3 Å in S_2Br_2). The equatorial C–S bond length is 1.730 ± 0.02 Å as compared with 1.695 Å in **1**.[7] It should be noted that **3** participates via a nonplanar geometry ($\zeta = 90.0°$) in the interaction qualitatively described in Figure 2, presumably due to the steric effect of the C-5 and C-4 methyl groups. Had planarity been possible, an even more stable structure should have resulted. Analogous tricoordinate sulfuranes, **3b**, mp 157–158 °C dec and **3c**, mp 147–150 °C

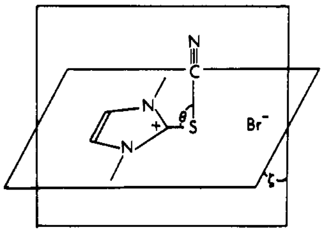

Figure 5. Solid state structure of salt **4a.**

dec, result from the reaction of **1** in CH_2Cl_2 solution at 0 °C with chlorine and iodine monobromide, respectively. The latter sulfurane begins to decompose in the solid state after ca. 1 h at room temperature which, nevertheless, represents extraordinary thermal stability considering the low dissociation energy of a normal two electron S-Br and S-I bond which here has an even lower bond order.

In contrast, the reaction of **1** with cyanogen bromide give the salt **4a,** mp 220-221 °C dec, whose crystal structure was determined similarily by x-ray diffraction: monoclinic; a = 7.288, b = 9.502, c = 15.206 Å; β = 122.459°; V = 1053 Å^3; Z = 4; ρ_{calcd} = 3.381 g/cm^3; space group $P2_1/C$ from systematic absences. A total of 1248 nonzero reflections were refined to a crystallographic R factor of 0.043 and the resultant structure is shown in Figure 5.

The covalent attachment of the cyano group is characterized by an axial S-C bond length of 1.757 Å orthogonal (θ = 96.20, ζ = 90.0) to the ring system while the equatorial bromide ion occupies a lattice position 3.270 Å distant from sulfur. A second neighbor bromide ion was found at a lattice position 3.587 Å in the axial direction from C2 anti to the cyano group.

Treatment of **1** with cyanogen chloride gives **4b,** mp 215-216 °C dec and the common ionic structure of these derivatives was evident from their superimposible IR spectra.

The observed incongruity between the appearance of a hypercovalent or an ionic molecule as a function of ligand structure is clearly independent of ligand electronegativity. If one considers an *electron-rich linear* multicenter bonding array with the hypervalent center participating by predominately p-orbital bonding two general patterns of occupied, symmetry-adapted, delocalized molecular orbitals appear. For $2n + 3$ (n = 0, 1, 2, . . .) atomic orbitals combined to give molecular orbitals with $2n + 4$ electrons there are $1n + 1$ occupied *nonbonding* levels with respect to the ligands which do not contribute to vicinal bonding in the array and for isolable hypervalent molecules requires electronegative ligands to stabilize the resultant electron density as is observed for **3.** Conversely, $2n + 4$ atomic orbitals combined to give molecular orbitals for $4n + 6$ electrons result in $4n + 2$ occupied *antibonding* levels noded with respect to the ligands which are destabilizing regardless of ligand electronegativity, as for example, the hypervalent possibility related to **4.** In other words, if the sum of the one central hypervalent atom plus the coaxial ligand atoms is odd the system is stable and, if even, destabilized. This argument may be extrapolated to account for the origin of the unusually high energy barrier observed for the gas-phase nucleophilic displacement at carbon associated the reaction of CN^- with CH_3Cl and C_2H^- with CH_3F which requires a linear transition state described by a combination of $2n + 4$ atomic orbitals.[7] Likewise the observed highly concerted decomposition (ΔH^* = 17.6 kcal/mol) of di-*tert*-butyl *O,O'*-phenylbisthioperbenzoate proceeds via a linear 6-electron 5-center hypervalent sulfur bonding array with one occupied bonding and two occupied nonbonding levels in the transition state and is an example of a stabilized $2n + 3$ atomic orbital combination.[8]

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Laser-Induced Lanthanide Ion Luminescence Lifetime Measurements by Direct Excitation of Metal Ion Levels. A New Class of Structural Probe for Calcium-Binding Proteins and Nucleic Acids

Sir:

The employment of the fluorescence of organic groups in biochemical research is widespread. In marked contrast, the use of metal ion luminescence in probing structure–function relationships remains a relatively unexploited area. Of all the metallic aquo cations in the periodic table, only certain members of the trivalent lanthanide series, Ln(III), luminesce in solution at room temperature. While Ln(III) ions do not occur naturally in biological systems, they appear to be, in general, capable of replacing calcium ions in biological systems[1,2] with isomorphous substitution having been demonstrated in several instances.[3,4] Unfortunately, in comparison to organic fluorophores, lanthanide ions are only weakly luminescent, principally because they are extremely weak absorbers of electromagnetic radiation. Heretofore, utilization of Ln(III) ion luminescence in biochemical research has been limited to cases in which the metal ion luminescence is greatly enhanced upon binding to a macromolecule. Only for Tb(III) bound to globular proteins[5-8] and for Tb(III) and Eu(III) bound to nucleic acids[9,10] have such intensity enhancements been reported. This enhancement of luminescence results primarily from energy transfer from strongly absorbing organic moieties (aromatic amino acids, nucleotide bases) to excited metal ion levels. The present report represents the initial stage of a program designed to extend the utility of Ln(III) ion luminescence to any macromolecule which binds a Ln(III) ion. The technique described, which does not depend on energy transfer, should allow additional members of the lanthanide series to serve as useful probe ions. The experiments are carried out using radiation of a wavelength at which most proteins and nucleic acids are transparent. We have concentrated initially on the measurement of Ln(III) ion luminescence decay constants which provide a sensitive measure of the number of water molecules coordinated to the metal ion.

In this study we exploit the large photon flux available from a coaxial flashlamp-pumped dye laser (Phase-R, Model 1200