Photoelectron Spectra and Electronic Structures of Trifluoramine Oxide and Trifluorophosphine Oxide

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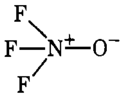
Abstract: Photoelectron spectra have been measured for F_3NO and F_3PO, and semiempirical molecular orbital calculations have been made for F_3NO to guide the interpretation of the ionization potentials. Approximate valence-bond calculations for the XO fragments of molecules of type Y_3XO indicate when X is N or P that minimum basis sets of Slater-type orbitals with free-atom exponents will need at least the addition of the 3d orbitals in order to predict charge distributions reliably. The vibrational spacing (1010 cm^{-1}) on the first band in the spectrum of F_3NO is discussed, although unambiguous assignment is not possible.

Trifluoramine oxide[1-4] poses an intriguing problem for bonding theory. In the valence-bond model, the electronic wave function can be considered to involve a combination of functions corresponding to structures such as I and II which maintain the valence-shell octet at nitrogen. However, comparison with F_3PO, which is valence isoelectronic with F_3NO, may suggest that the structure III involving nitrogen in the pentavalent state could contribute also. The extent of the participation of structures of type III for F_3PO has been debated for many years, but the most recent theoretical and experimental evidence for related molecules of phosphorus and sulfur suggests that the involvement of 3d orbitals in F_3PO is likely to be substantial. The nonempirical molecular orbital calculations by Hillier and Saunders[5,6] on SO_2 and SO_4^{2-} show 3d electron populations of 1.17 and 2.58, respectively, and the photoelectron spectra of the cyclic phosphonitrilic fluorides are also suggestive of important 3d orbital interactions.[7] In addition, approximate calculations[8] have indicated a mechansim whereby the 3d orbitals, which have high energies and diffuse radial forms in the free phosphorus atom, can be stabilized sufficiently in the molecular environment of F_3PO to allow significant participation in bonding models.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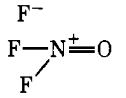
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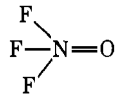
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In F_3NO, the N–O bond is 0.26 Å shorter than the N–O single bond length (1.42 Å) and the N–F bonds are 0.05 Å longer than usual for an N–F single bond (1.38 Å),[9,10] At present it is not clear whether the lengthening of the N–F bonds indicates the importance of contributions by the structures II or whether it is simply that the "natural" N–F single bond for four-coordinate nitrogen is longer than that for nitrogen exhibiting the more usual coordination numbers. In any event the shortening of the N–O bond length is suggestive of double-bond character. Bartell, *et al.*,[11] have noted some similarities in the trends of bond lengths in F_3NO, F_3PO, and related molecules, and this suggests that there may be similarities in the valence-shell electronic distributions in the NO and PO bonds.

To provide the basis for further discussions of the electronic structures of F_3NO and F_3PO, we have determined their ionization potentials by photoelectron spectroscopy, using the experimental techniques described recently,[12] and we have made some theoretical calculations.

Results and Discussion

Photoelectron Spectra. The photoelectron spectrum of F_3NO in Figure 1 shows evidence for four ionization potentials, and the photoelectron spectrum of F_3PO in Figure 2 shows evidence for six ionization potentials. The adiabatic and vertical values for both molecules are given in Table I.

Table I. Ionization Potentials (eV) of F_3NO and F_3PO

F_3NO			F_3PO		
Adiabatic	Vertical	Vibrational spacing, cm^{-1}	Adiabatic	Vertical	Vibrational spacing, cm^{-1}
13.51[a]	14.26	1010	12.75	13.53	
15.1[b]	15.63		15.25	15.70	
16.5[b]	17.33		16.70	17.11	
20.0	20.33		17.3[b]	17.84	
			18.45[b]	18.91	740
			19.3[b]	19.68	740

[a] See text. [b] Upper limit, since adjacent bands overlap.

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[1] N. Bartlett, J. Passmore, and E. J. Wells, *Chem. Commun.*, 213 (1966).

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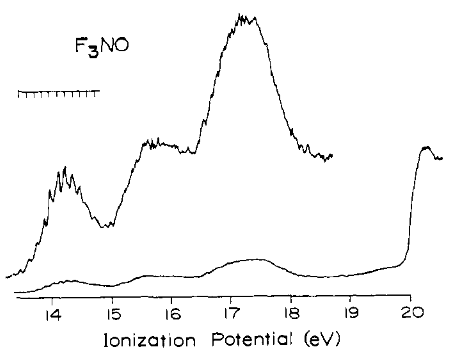

Figure 1. Photoelectron spectrum of F_3NO.

For F_3NO, the first ionization potential of 13.51 eV is to be compared with 13.26 eV, the photoionization value of Dibeler and Walker.[13] The vibrational spacing we obtain for this band is 1010 cm^{-1} (0.125 eV), and two quanta of vibrational energy less than the ionization potential we observe brings the value to 13.26 eV, in exact agreement with the value of Dibeler and Walker. This suggests that the first vibrational level we observe corresponds to $v = 2$, the first two members of the progression being of too low intensity to be detected. The vibrational spacing on this band is discussed further below.

Molecular Orbital Calculations. Recently there have been indications that the lower ionization potentials of molecules of first-row atoms can be predicted to within 1 eV with the semiempirical molecular orbital methods, provided there is an additional empirical correction which amounts to decreasing the energy zero by 4 eV.[14-16]

For F_3NO, we have used as a basis the atomic orbitals of the second quantum shells and we have simplified the molecular integrals according to the incomplete neglect of differential overlap (INDO) scheme,[17] using a molecular geometry (symmetry C_{3v}; N-F, 1.44 Å; N-O, 1.17 Å; ∠FNF, 102°; ∠ONF, 117°) close to that from electron diffraction.[9] The calculated vertical ionization potentials for F_3NO are (eV) 12.43 (symmetry species e), 16.60 (a_1), 17.40 (e), 18.04 (a_2), 18.79 (e), and 20.65 (a_1). These calculated values may be compared with the experimental values in Table I. The agreement is not as good as is often found with the INDO method for molecules of first-row atoms; thus, for the first ionization potential, the calculated value is too low by 1.8 eV. According to the INDO calculation, the first ionization corresponds to the removal of an electron from a molecular orbital with a large contribution from oxygen, the electronic distribution for this orbital being $(F^{0.12})_3N^{0.00}O^{0.65}$. A population analysis for the complete INDO wave function shows the net charges in F_3NO to be $(F^{-0.19})_3N^{+0.90}O^{-0.33}$. The calculated dipole moment (0.80 D) shows a larger discrepancy from the experimental value (0.039 D)[18] than is typical for molecules containing first-row atoms.[17]

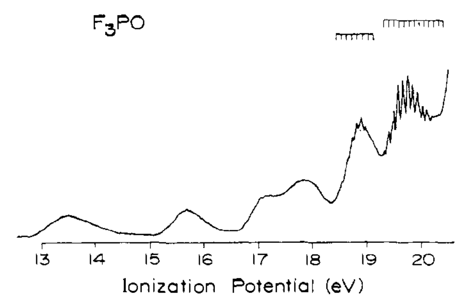

Figure 2. Photoelectron spectrum of F_3PO.

Vibrational Structure. The origin of the vibrational spacing (1010 cm^{-1}) on the first band in the spectrum of F_3NO is of some interest. Since the first ionization is likely to involve the removal of an electron from an e-type molecular orbital which is centered mainly on oxygen, it is probable that the symmetry of the molecule is maintained in the ground state of the positive ion; however, changes in bond lengths almost certainly occur, as evidenced by the long vibrational progression on the first band. The vibrational structure is likely to originate from one of the totally symmetrical modes of the molecule, namely ν_1, ν_2, or ν_3 (Table II).

Table II. Vibrational Frequencies (cm^{-1}) of F_3NO and F_3PO

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
F_3NO^a	1691	743	528	883	558	398
F_3PO^b	1415	873	473	990	485	345

[a] References 2 and 3. [b] H. S. Gutowsky and A. D. Liehr, *J. Chem. Phys.*, **20**, 1652 (1952).

The INDO calculation indicates a negligible electron density at nitrogen in the highest occupied molecular orbital, and therefore that this orbital is essentially nonbonding both between nitrogen and oxygen and between nitrogen and the fluorines. On this basis the symmetrical stretching frequencies would be expected to be changed only slightly from the values for the neutral molecule. If higher atomic orbitals of e symmetry are involved significantly at nitrogen, the overlaps in the highest occupied molecular orbital become bonding both between nitrogen and oxygen and between nitrogen and the fluorines, and then both ν_1 and ν_2, respectively the NO and NF stretching frequencies, would be expected to be less in the positive ion than in F_3NO. This seems to rule out ν_2, which is 743 cm^{-1} in the neutral molecule. In addition, Dibeler and Walker[13] observe the appearance potential of F_2NO^+ at 13.59 eV, and this may preclude a vibrational progression involving the NF stretching frequency.[19] The vibrational structure could

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(19) We are grateful to a referee for a possible reconciliation of the photoionization and photoelectron results in terms of ν_2. Fragmentation observed at low energies usually occurs by way of an asymmetric vibrational mode. The weak F_3NO^+ current starting at 13.26 eV and followed closely by the strong F_2NO^+ onset at 13.59 eV probably represents transitions to the same ionic state. Vibrational levels of F_3NO^+ populated by direct Franck-Condon transitions are represented by the vibrational series observed in the photoelectron spectrum. This has its dissociation limit at least as high as 14.8 eV. Within the time scale of the mass spectrometer (10^{-5} sec; *cf.* 10^{-14} for photoelectron spectroscopy), the vibrational energy above 13.59 eV could be transferred to the vibrational mode that gives F_2NO^+. This mode has its dissociation limit at 13.59 eV. In other words, the ionic potential surface

arise from ν_1 if there are substantial bonding interactions between nitrogen and oxygen in the highest occupied molecular orbital, although the reduction from 1691 to 1010 cm^{-1} is large. It may be noted that NO stretching frequencies[20] in the organoamine oxides (R_3NO) are between 950 and 970 cm^{-1}, and therefore, since ν_1 is sensitive to the particular environment, it is conceivable that ν_1 for F_3NO could show a large change in value on ionization corresponding to a weakening of the NO bond. If this is the reason for the vibrational spacing of 1010 cm^{-1} the NO bond length in F_3NO^+ would be expected to approach the value of 1.44 Å in $(CH_3)_3NO$.[21]

In other C_{3v} molecules such as CH_3CN, CH_3CCH, and CH_3Br, isotope substitution studies have confirmed[22,23] that the ions produced by removal of an electron from the highest occupied e-type molecular orbital show vibrational progressions involving the symmetric CH_3 deformation mode. For the symmetric NF_3 deformation to be the origin of the vibrational progression in F_3NO^+, it would be necessary to accept an approximate doubling in the frequency of ν_3. It is not understood how this could occur, but changes of this magnitude have been observed in the tetraatomic group V hydrides and halides,[24,25] although in these cases the frequencies in the ions are about half of the frequencies for the neutral molecules. If the distortions in the ion are sufficiently large and asymmetric that the C_{3v} model loses its validity, then the asymmetric vibrations could in principle be involved, although the assignment is no easier than for the symmetric vibrations.

Dibeler and Walker's observation[13] that the appearance potential of F_2NO^+ is 13.59 eV suggests that we may be observing a different process from that giving F_2NO^+, and there is the possibility that the photoionization results involve an ion-pair process. The INDO calculation gives no indication of another ionic state in the region of the first band in our photoelectron spectrum; however, we do observe only four ionization potentials for F_3NO, whereas the INDO calculation predicts six in our observable range. This cautions us to note that there may be additional ionizations to the ones we observe in the spectrum of F_3NO. For example, if there are large geometry changes in some ionic states, the intensities in the photoelectron spectrum would be low and these peaks could be overlapped and masked by bands of higher intensity.

Vibrational structure is clearly exhibited on the 18.3- and 19.3-eV bands of F_3PO. In each case the frequency involved is 740 cm^{-1}, which probably corresponds to the symmetric stretching vibration (ν_2) whose frequency is 873 cm^{-1} in the neutral molecule.

The Involvement of Excited Orbitals. The principles currently believed to govern 3d orbital bonding by atoms of the second row[26,27] can apply also to first-row atoms such as nitrogen. An indication that the 3d orbitals at nitrogen could be involved in F_3NO is provided by the molecular orbital calculations made by McLean and Yoshimine[28] for N_2O using an extended basis set. The $3d_\pi$ contributions are greatest for the central nitrogen atom and the $2p_\pi(N')$–$3d_\pi(N)$ and $3d_\pi(N)$–$2p_\pi(O)$ overlap populations are 0.212 and 0.251, respectively, for the 2π molecular orbital. These overlap populations are several times the overlap population (0.089)[28] for the 1π molecular orbital of HF, and it may be noted that Mulliken[29,30] first proposed bonding interactions of the hydrogen $2p_\pi$ atomic orbitals in diatomic hydrides to account for the experimental observations that the bond lengths of diatomic hydrides increase on ionization.

The considerations of prime importance now concern the effect of 3d orbital involvement at nitrogen on the electronic distribution and energy of wave functions for F_3NO and on the comparison with F_3PO.

Extended Valence-Bond Calculations. In order to gain a preliminary estimate of the effect of 3d orbital involvement in NO and PO bonds, we have made some model calculations[31] based on the extended valence-bond method.[32] The calculations restrict consideration to the fragment XO (X is N or P) and assume a core specified for the valence-shell orbitals by $h_1^{(1-q)}h_2^{(1-q)}h_3^{(1-q)}$ at X and $2s^2$ at O. The other atoms (*i.e.*, the fluorines in F_3NO and F_3PO) are not explicitly included, although they are considered to act as a sink for accepting an amount q of electronic charge from each of the three equivalent sp^3 hybrids (h_1, h_2, and h_3) at X. The electronic wave function of the XO fragment is an antisymmetrized product of three two-electron functions which describe the overlap of h_4 (the fourth and nonequivalent sp^3 hybrid) at X with the $2p_z$ orbital at O, the overlap of $3d_{xz}$ at X with $2p_x$ at O, and the overlap of $3d_{yz}$ at X with $2p_y$ at O. The form of the two-electron function ψ_i for bond i is

$$\psi_i(1,2) = N_i[(\psi_{Xi} + k_{+i}\psi_{Oi})(1)(\psi_{Oi} + k_{-i}\psi_{Xi})(2) + (\psi_{Xi} + k_{+i}\psi_{Oi})(2)(\psi_{Oi} + k_{-i}\psi_{Xi})(1) \quad (1)$$

where N_i is the normalization cons ant, ψ_{Xi} and ψ_{Oi} are the overlapping orbitals at X and O, and k_{+i} and k_{-i} are related to an ionic character parameter k_i ($-\infty \leqslant k_i \leqslant \infty$) by

$$k_{+i} = 0.5(|k_i| + k_i)$$

$$k_{-i} = 0.5(|k_i| - k_i)$$

When k_i is positive, the electron density of the bond is polarized toward O and when k_i is negative, the bond density shifts toward X.

The valence-shell orbitals of the core are orthogonalized to all inner orbitals by the Schmidt method, and the bonding orbitals are completely orthogonalized to the core. For this situation the energy of the antisymmetrized wave function for the three electron pairs has been given in general form by Hurley, Lennard-Jones, and Pople.[32] The calculations are made using Slater-type

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possesses a deep "lip" in it, allowing a fragmentation channel. Autoionization could enhance the production of F_3NO^+ below 13.59 eV.

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orbitals with exponents given by Clementi and Raimondi.[33] For PO the 3d exponent is fixed at 1.40, as recommended by Boyd and Lipscomb,[34] and this value is used also for the 3d orbitals at nitrogen in NO. The one-electron integrals are evaluated accurately by numerical methods, and the approximations in the two-electron integrals amount to the use, as in eq 2, of the Mulliken approximation[35]

$$\langle \mathrm{ab}|\mathrm{ab}\rangle = 0.5S_{\mathrm{ab}}[\langle \mathrm{aa}|\mathrm{ab}\rangle + \langle \mathrm{bb}|\mathrm{ab}\rangle] \qquad (2)$$

for a single overlap distribution in an electron-repulsion exchange integral. The angle of the sp^3 hybrids at X and the XO bond distance are chosen to conform to the molecular geometries of F_3XO.[9,36] The electronic energies of the NO and PO fragments are minimized by varying the ionic character parameters for both the σ and π bonds, and the results are given in Table III for q = 0, 0.30, and 0.60 for the two bonding models corresponding to the neglect and to the inclusion of the $3d_\pi$ orbitals at X.

Table III. Results of Extended Valence-Bond Calculations for NO and PO

Molecule	q	3d orbitals	Optimized ionic character parameters k_σ	k_π	$3d_\pi$ population	Energy, au
NO	0	Neglected	−0.74	∞	0	−11.01
		Included	−0.53	1.15	0.90	−11.30
	0.30	Neglected	−1.19	∞	0	−13.44
		Included	−0.85	1.11	0.93	−13.75
	0.60	Neglected	−1.97	∞	0	−15.90
		Included	−1.37	1.07	0.95	−16.22
PO	0	Neglected	−0.80	∞	0	−9.79
		Included	−0.38	0.99	1.01	−10.11
	0.30	Neglected	−1.02	∞	0	−11.55
		Included	−0.45	0.87	1.10	−11.91
	0.60	Neglected	−1.31	∞	0	−13.31
		Included	−0.53	0.78	1.18	−13.72

The substantial drift toward X in the σ bonds for both models of bonding is deceptive since the σ hybrids at X are heavily contaminated by oxygen 2s orbitals from the orthogonalization procedures,[37] but it is a sensible result that the apparent drifts toward X in the σ bonds are less for the models that include $3d_\pi$ orbitals. Both the 3d electron populations and the energy gains from including 3d functions are slightly greater for PO than NO for a given value of q, but the new result is that there is no sharp difference between NO and PO in relation to 3d-orbital participation.[38] This suggests that the electronic distributions in F_3NO and F_3PO are not fundamentally different, although, for the basis set used here, it seems inevitable that the 3d-orbital contributions are larger in F_3PO than in F_3NO, especially because considerations of atom electronegativities[10] indicate that the appropriate value of q would be larger for the phosphorus compound.

Additional calculations have also been made for the model where the $3d_\pi$ orbitals are replaced by the $(n + 1)p_\pi$ orbitals, but the contributions by these latter orbitals are found to be always small, the electronic distributions being only slightly changed from when the involvement of excited atomic orbitals is neglected. This small involvement by the outer p orbitals at X is a consequence of the necessity to orthogonalize these orbitals to the conventional valence shell; by contrast the $3d_\pi$ orbitals at X are automatically orthogonal to the s and p valence orbitals, and the constraining influences on the overlap with $2p_\pi$ orbitals at oxygen are much less.

Concluding Remarks

Even though the extended valence-bond calculations reported here are idealized in that they apply only to fragments of actual molecules, these calculations do nevertheless indicate strongly that minimum basis sets of Slater-type orbitals with free-atom exponents will need the addition of 3d orbitals for application to F_3NO, F_3PO, and related molecules. This conclusion is consistent with the discrepancies between theory and experiment that we find with the INDO calculations of F_3NO, although a definitive statement is not possible, especially because the ability of the INDO method to predict molecular properties has not yet been exhaustively studied. However, our findings do tie together in a qualitative sense. Thus the INDO calculation indicates a large positive charge at nitrogen and this is consistent with substantial contributions from the valence-bond structures I and II. On the addition of $3d_\pi$ orbitals, it seems probable that the electronic density around oxygen will be remolded and diffused toward nitrogen so that electron repulsions at oxygen are reduced. This leads us to believe that the addition of 3d orbitals to the INDO calculations would lead both to an increase in the calculated value of the first ionization potential and to a less extreme charge distribution, and the latter may lead to a lower calculated dipole moment. This suggests a consistent framework, but the question of whether 3d orbital involvement is essential in the molecular orbital model can only be answered by minimizing the molecular energy through a complete variation in the basis of s, p, and d orbitals.[39]

Our model calculations highlight the effect of the oxygen atom on the 3d orbitals of X, but for actual molecules of type Y_3XO the atoms Y must have a significant influence also. It is important to note that the 3d orbitals with π symmetry with respect to the XO bond have appreciable σ character relative to the XY bonds,[40] and this will lead to additional stabilization of these 3d orbitals when the atoms Y are highly electronegative and are able to get a large effective nuclear potential close to the radial maxima of the 3d orbitals.[41,42] In this regard, fluorine is likely to be more efficient than carbon at enhancing the stabilization of the 3d orbitals, and for this reason we expect the involvement of 3d

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(37) The ratio of the coefficients for N 2s and O 2s Slater-type orbitals in the orthogonalized form of the bond hybrid at N in NO is 1.000 to −0.800.

(38) In ref 34 Boyd and Lipscomb show the importance of 3d orbitals in small phosphorus molecules when free-atom exponents are used for the s and p Slater-type orbitals.

(39) K. A. R. Mitchell, *Inorg. Chem.*, **9**, 1960 (1970).

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orbitals at nitrogen to be more important in F_3NO than in $(CH_3)_3NO$.

Finally it may be noted that this viewpoint is not fundamentally different from the alternative[4,20] that ascribes the stability of F_3NO, and the differing properties of NO bonds in F_3NO and in the organoamine oxides, to the double bonding resulting from the back-donation of lone pairs on oxygen into antibonding σ orbitals associated with the NF bonds. The relation between these bonding models follows since the antibonding σ orbitals would presumably be expected to be associated with substantial 3d orbital contributions, and, as we noted earlier, the 3d orbitals with π symmetry with respect to the NO bond have appreciable σ character in the NF bonds.

Acknowledgments. We thank the National Research Council of Canada for financial grants, Dr. W. B. Fox of Allied Chemical Corporation for the generous gift of a sample of F_3NO, Professor K. Hedberg for communicating his electron diffraction results, Dr. R. C. Catton for his help with the computations, and Professor C. A. McDowell for his interest in this work.

Circular Dichroism of Nucleoside Derivatives. X. Influence of Solvents and Substituents upon the Cotton Effects of Guanosine Derivatives

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Abstract: The effects of certain substituents and solvents on the circular dichroism (CD) spectra are reported for a number of guanine nucleoside derivatives from 320 to 200 nm. Both theoretical and empirical analyses of the data suggest that the anti conformation predominates in aqueous solution, but that the syn conformation is preferred in alcoholic solvents, at low pH in water, and when the heterocycle carries a large substituent on carbon 8 of the imidazole ring. Theoretical optical calculations based on the bond-bond coupled oscillator theory are included to check the validity of the theory with experimental data. The interaction of guanine nucleoside derivatives with actinomycin is also reported and the data suggest that the anti conformation is necessary for complex formation.

A fundamental aspect of the conformational analyses of nucleic acids and their fragments concerns the allowed conformational states of the individual nucleotide or nucleoside monomers. In particular the relative position of the sugar and the base about the glycosidic bond, as described by the torsion angle, ϕ_{CN}, has received a great deal of attention.[1-4] Steric considerations lead to two extreme conformations as demonstrated by **1** and **5** in Figure 1, which are designated anti and syn, respectively. Crystallographic studies have pointed to the almost exclusive presence of the anti conformation.[5] A number of exceptions, however, are known: deoxyguanosine, which is syn in a mixed crystal with 5-bromodeoxycytidine;[6] 3′,5′ cyclic AMP, which can exist simultaneously in the anti and syn conformations in the same crystal structure;[7] 8-bromoguanosine;[8] 8-bromoadenosine;[8] and 3′-*O*-acetyladenosine.[9] Several independent calculations using the criteria of potential energy conclude that in purine nucleosides the free energy difference between the syn and anti states is small.[10-12] Finally, several nmr studies have implicated the anti conformation as predominating in solutions.[13,14]

We now report the effects of substituents, pH, and solvent on the CD spectra of certain guanosine derivatives. Despite measurements on numerous derivatives under diverse conditions, much of the data can be understood in terms of two basic spectra which may approximate the characteristic spectra of a pure anti conformational distribution and a pure syn conformational distribution. The circular dichroism curve of a guanosine derivative having a conformational distribution entirely in the syn range is likely quite well represented by the CD spectra of the six derivatives featuring a bulky 8 substituent. To provide a guide for interpretation of the data in terms of molecular con-

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