Conformational Analysis of Phosphazenes. A Force Field for the Calculation of the Molecular Structures of Halophosphazenes

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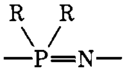
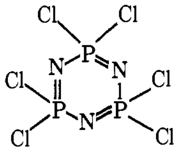
Abstract: Phosphazenes ($-N{=}PR_2-$) are a series of compounds that include rings of various sizes and conformations and linear high molecular weight polymers. The bonding in this system is interesting, since the formal valence structure presents the possibility of π-electron delocalization. In the present work an attempt was made to see if phosphazene properties could be accounted for in terms of a conventional conformational model in which the molecules are subject to the influences of the energetics of bond twisting, bending, and stretching (and nonbonded interactions), but in which there are no further effects on bonding in various size molecules than from these sources (i.e., the individual bond energies do not depend on the size of the molecule). It was found that the geometries, energies, and vibrational frequencies of a number of cyclic perhalophosphazenes could be satisfactorily accounted for by such a model. A force field for conformational calculations on chloro- and fluorophosphazenes is presented. Important and necessary features of the model include a twofold torsional potential with a low barrier (~1.4 kcal/mol) and a soft bending constant at the PNP valence angle (both absolutely and relative to the NPN angle).

The phosphazene moiety (I) is the basis of a group of compounds that are of considerable interest in structural chemistry and in chemical technology.[1-6] In the formal valence structure the phosphorus and nitrogen bonds alternate as single and double bonds. It has been the subject of some speculation and study as to what extent and in what manner delocalization takes place in this conjugated system.[5,7] The phosphazenes include a variety of cyclic oligomers whose structures are of interest in the question of the nature of the bonding.[5] They also exist as linear high molecular weight polymers that have quite low glass temperatures and are elastomeric when noncrystalline.[5,6] Other polymers with appropriate substituents (R groups in I) are semicrystalline thermoplastics. Both groups of polymers show considerable promise as technologically important materials.[6]



I

The nonalternation of bond lengths in compounds like II leaves no doubt that the formal valence structure does not represent the actual structure. The π-electron system may be in some way delocalized.[5,7] If the phosphorus role in the π system is dominated by d_{xz} orbital (lobes normal to the ring xy plane and tangential to the ring perimeter) participation, then it may be expected that broad delocalization would occur but be "pseudoaromatic" in character. However dominance by d_{yz} (lobes radial to the ring perimeter) participation would lead to broad delocalization more similar to that found in aromatic systems involving p_π–p_π orbitals. Equal participation of d_{xz}, d_{yz} orbitals would result in delocalization confined to NPN sequences or "islands". The wide variety of nonplanar geometries of other cyclic oligomers and the solution flexibility and low glass temperatures of the linear high polymers indicate that there is not an excessive requirement for planarity of the PN skeleton for effective overlap in the π system and therefore there is not an excessively high barrier to rotation about the PN bonds. In fact, Allcock,[5,8] noting the low glass temperatures of the linear polymers, has speculated that d-orbital participation from the phosphorus atoms results in a diffuse cylindrically symmetrical electron distribution about the PN bond that leads to a virtually zero barrier to rotation. Another possibility is that there is no π bonding and that the ring bonds are actually single bonds.[43] Although the relation between the barrier to skeletal bond rotation and glass temperature is not clear and there are examples of reasonably high barriers associated with low glass temperatures,[9] it nevertheless seems of considerable interest to investigate further the questions of the torsional barrier in phosphazenes.



hexachlorocyclotriphosphazene
II

The study of the relation between intrinsic atomic (and bond) properties and molecular structure has in general been aided in recent years by semiempirical conformational energy calculations. That is, if a molecule may be regarded as assembled from groups of atoms and bonds whose intrinsic properties are independent of the particular molecule being built, then its molecular properties can be calculated from energy functions describing its atoms and bonds. If functions describing nonbonded interactions between atoms, torsional barriers, valence angle deformations, and bond stretching are known, the geometries and energies of various conformations and the energetics of paths for transitions between conformations may be calculated. The applicability of the model (i.e., the validity of the approach) and the parameters in the energy functions are decided on by calculations on a basis set of appropriate compounds for which a variety of information concerning molecular geometries, energies, and other properties is experimentally available. Since molecular vibrations involve similar deformations to those in assembling strained molecules (torsion, bending, stretching), vibrational spectra have been of great assistance in determining the appropriate energy parameters (i.e., force field). The approach has been remarkably successful for a variety of organic compounds where the assumptions of the model are valid.[10,11] That is, almost any geometrical deformation of bonds (strain) is allowed, but electronic delocalization effects are presumed not to change over those effects in the groups of bonds used for assembly of the molecule.

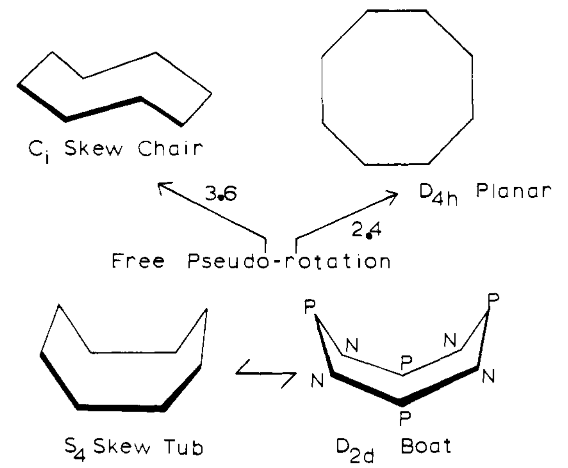


Figure 1. The hexachloro cyclic tetramers and the calculated energetic relationships among them as isolated molecules. The skew tub and boat interconvert by a free pseudorotation. The other forms lie at higher energy by the amounts shown (in kcal/mol). The pseudorotation involves the boat form shown, with the P atoms occupying the out-of-plane positions. The alternative D_{2d} form with the N atoms occupying these positions is calculated to be less stable.

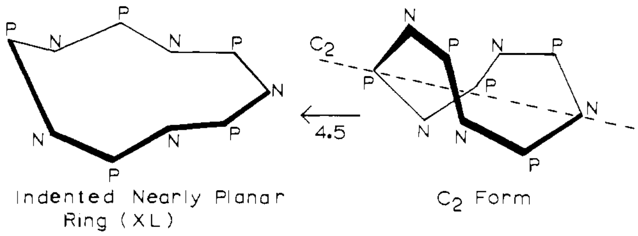


Figure 2. Two decachloro cyclic pentamers and the calculated energetic difference between them (kcal/mol).

The availability of a reasonably large body of experimental information on the geometries, vibrational spectra, and energies of halophosphazenes has prompted us to attempt the formulation of a force field for the calculation of their conformational properties and to investigate its applicability. The purpose of the present paper is to report the results of this investigation.

Data Base

The following information was used in developing the conformational model and force field.

1. Molecular Geometries. X-ray diffraction structures of the hexachloro[12] and hexafluoro[13] cyclic trimers, two modifications of the octachloro cyclic tetramer,[14,15] the octafluoro cyclic tetramer[16] and the decachloro cyclic pentamer,[17] and the linear dichloro[18] and difluoro[8] polymers were used. The cyclic trimers are very nearly planar with nearly D_{3h} symmetry.[12,13] The octachloro cyclic tetramer (Figure 1) is found in the two crystal modifications to be either a slightly skewed (S_4) tub[14] or a slightly skewed (C_i) chair.[15] The octafluoro cyclic tetramer is planar.[16] The decachloro cyclic pentamer (Figure 2) is an indented ring that is approximately planar around the indentations.[17] However the ring is bent upwards somewhat at that part of the ring farthest from the indentations.

2. Molecular Energies. The heats of polymerization of the perchloro cyclic trimer through heptamer have been measured calorimetrically by Jacques, Mole, and Paddock.[19] The heats of vaporization of these compounds are also available. In addition, the heats of vaporization allow the estimation of an incremental heat of vaporization of a monomeric unit in the linear polymer. Therefore a *vapor-phase* heat of polymerization can be determined. We *define* here an experimental strain energy, SE, of a cyclic *n*-mer as the negative of this vapor-phase heat of polymerization,

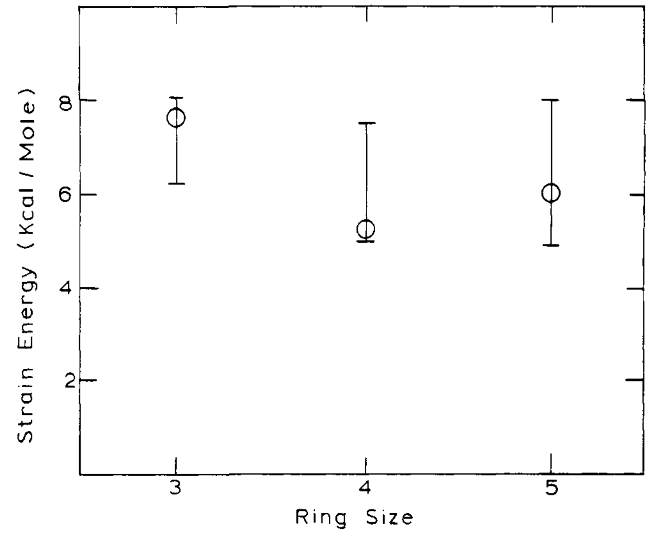


Figure 3. Experimental (vertical bars) and calculated strain energies (O) of perchlorocyclophosphazenes. The experimental values are based on vapor-phase heats of polymerization. The error bars for the experimental values are based on an assumed uncertainty of ±0.3 kcal/mol in the incremental heat of vaporization of the linear polymer (see eq 21). For the tetramer the calculated point is for the tub-boat (Figure 1) and for the pentamer it is for the C_2 form (Figure 2).

$$\boxed{+\text{NPCl}_2+}_n \xrightarrow{-\text{SE}} +\text{NPCl}_2+_n \qquad (1)$$

Thus,

$$-\text{SE} = \Delta H_p{}^\circ(n) + n\Delta H_v{}^\circ \text{ (linear increment)} - \Delta H_v{}^\circ \text{ (cyclic } n\text{-mer)} \qquad (2)$$

where $\Delta H_p{}^\circ(n)$ is the condensed phase heat of polymerization of a polymer with n units and $\Delta H_v{}^\circ$ are heats of vaporization. The value of 2.5 kcal/mol was taken for the linear increment.[19] We have assumed an uncertainty of 0.3 kcal/mol in this quantity to be reasonable. The experimental strain energies are shown in Figure 3. Calculated strain energies were determined by establishing an increment with chain length in the calculated conformational energies of a series of linear (planar cis-trans) oligomers. This increment multiplied by the mer number is subtracted from the calculated conformational energy of a cyclic *n*-mer to give a calculated strain energy.

3. Vibrational Spectra. The infrared and Raman spectra of the perchloro and perfluoro cyclic trimer and tetramer have been studied by a number of workers.[20-28] Manley and Williams[24] have summarized assignments[22,23] of the spectra of the hexachloro and hexafluoro cyclic trimers (and have made a complete assignment for the hexabromo cyclic trimer). They have also made a complete assignment for the octachloro (and octabromo) cyclic tetramer.[24,26] Hisatsune[25] has made a partial assignment of the octachloro cyclic tetramer and regards the complete assignment of Manley and Williams[24] as tentative. In fact it is probably fair to say that only for the hexachloro cyclic trimer is there consensus on anything approaching a complete assignment. As we shall see, we believe there are some problems there also.

The spectra of the cyclic trimers are in agreement with the x-ray findings of planar molecules with (nearly) D_{3h} symmetry. Both Manley and Williams[24,26] and Hisatsune[25] interpret the spectra of the octachloro cyclic tetramer as being most consistent with a D_{2d} (boat) form in the liquid phase or in solution. Hisatsune[25] observes simplification of the spectra in the vapor

Table I. Valence Force-Field Parameters for Halophosphazenes[a]

	Stretching[b] k	R_0
PN	5.9	1.57
PCl	2.8	1.99
PF	5.9	1.52

	Bending[c] k	k'	Θ_0
PNP	0.25	−0.072	2.2864 (131°)
NPN	0.90	0.0	2.1118 (121°)
NPCl	0.60	0.0	1.8850 (108°)
NPF	1.2	0.0	1.8937 (108.5°)
ClPCl	1.5	0.0	1.7802 (102°)
FPF	2.5	0.0	1.7436 (99.9°)

	Torsion[d] V_1	V_2
NPNP	0.00208	0.010

[a] To be used in conjunction with the nonbonded parameters of Table II. Units are such that energies are 10^{-11} erg/molecule, angles in radians, and distances in angstroms (i.e., conventional spectroscopic force constant units of 10^5 dyn/cm or mdyn/Å). To convert energies to kilocalories per mole multiply by 144.0. [b] Harmonic function. [c] Equation 4 of text. [d] Equation 3 of text.

phase (especially disappearance of the 890-cm^{-1} infrared band) which he interprets as an increase in symmetry to the D_{4h} planar form.

Conformational Model

The basic particular assumption of our model as applied to phosphazenes is that the torsional barrier is twofold (with a height to be determined by matching calculated results with experiment). That is only cis and trans states of the NPNP sequence have inherently stable minima. This assumption was initially prompted by the theoretical expectation that maximum torsional stability will be associated with maximum orbital overlap in these two planar conformations and by the experimental fact[8,18] that the linear open chain strain free polymers (dichloro and difluoro) prefer the alternating cis-trans planar (or nearly so) conformation. During the course of the calculations, inclusion of threefold barrier contributions were experimented with, but no improvement of results was noticed. However, we did find somewhat better fit of the oligomer stabilities (Figure 3) by including a slight cis-trans energy difference. This was represented by a single-fold contribution to the potential.[29] Thus our rotational barrier is of the form,

$$V(\phi) = V_1/2(1 + \cos\phi) + V_2/2(1 - \cos 2\phi) \qquad (3)$$

(where $\phi = 0$ for the cis state, 180° for trans and $V(180°) = 0$).

Since complete vibrational assignments of the perchloro cyclic trimer (II) are available,[22,24] we had hoped at the onset to be able to arrive at the value of the torsional barrier from the out-of-plane frequencies. However, as we will see there are complications that prevent this and the barrier must be determined from the stabilities and geometries of the cyclic oligomers.

As indicated above, the cyclic oligomers take on an interesting array of conformations. The most impressive feature of these conformations is the remarkable range of values found for the PNP valence angle. It varies from ~122° in the cyclic trimers,[12,13] to 131–137° in the puckered octachloro cyclic tetramers,[14,15] to 147° in the planar octafluoro cyclic tetramer,[16] to ~158° at the indentation in the decachloro cyclic pentamer.[17] The NPN angle is subject to much less variation. At first glance (based on experience with medium sized hydrocarbon rings) it might seem difficult to accommodate these extreme variations in a building block conformational model. However, it seemed possible that by making the PNP bending constant much softer than the NPN constant such effects might be reproduced. It was also considered likely that over such wide ranges of valence angle the effective force constant for PNP bending would change. In the course of the calculations it was found that allowing the force constant to decrease with increasing valence angle gave a better representation of structures and stabilities. This was accommodated by an anharmonic potential of the form

$$V(\theta_{\mathrm{PNP}}) = (k/2)(\theta - \Theta_0)^2 + k'(\theta - \Theta_0)^3 \qquad (4)$$

The adjustment of the force constants (other than the torsional barrier and the PNP bending constants) was largely made by optimizing the fit to the spectra of the cyclic trimers (by successive relaxation of the constants). In the course of this adjustment it was found that because of the high masses of the substituents (compared to hydrogen) and in contrast to hydrocarbons, the frequencies of nearly all modes depended heavily on several force constants. It was generally not possible to describe the vibrations in terms of group motions such as "PCl_2 rocking" or "out-of-plane ring deformation", etc.

The exceptions to the constants being determined from the trimer spectra were the torsional barrier, the anharmonic constant k' (eq 4) in the PNP bending function, a final adjustment of the PNP harmonic constant k (eq 4) and the nonbonded parameters. The torsional barrier was determined by optimizing the fit of the stabilities of the perchloro cyclic oligomers. It was found in fitting the spectra that the calculated frequencies were not very sensitive to the individual PNP and NPN bending constants, but rather to their mean. Thus there was considerable latitude in varying the ratio of these constants, but once the ratio was fixed the spectra imposed bounds on their values. The ratio of the bending constants was largely determined by the geometries of the hexachloro cyclic trimer (118.4° NPN and 121.4° PNP[12]) and the planar octafluoro cyclic tetramer (122.8° NPN and 147.1° PNP[16]). The anharmonic PNP constant (k', eq 4) was largely determined by the requirement that the planar tetramer be comparable in stability to puckered tetramers, by the experimental PNP angles in the planar perfluoro cyclic tetramer, and by the necessity of reaching very large PNP deformations (up to ~158°) in the decachloro cyclic pentamer without undue strain energy. Although the spectra place bounds on k_θ(PNP) once the ratio of bending constants is fixed, a final adjustment could be made based on the stabilities of the cyclic oligomers. A fixed value for the relaxed PN bond distance (1.57 Å) in all compounds was adopted. The justification for this will be taken up in the Discussion.

The valence force-field parameters arrived at are summarized in Table I.

The nonbonded functions used were of the form

$$V(R) = A\exp[-BR] - C/R^6 \qquad (5)$$

or its equivalent,

$$V(R) = \frac{\epsilon}{1 - 6/\alpha}\left[\frac{6}{\alpha}\exp[\alpha(1 - R/R_{\mathrm{m}})] - \left(\frac{R_{\mathrm{m}}}{R}\right)^6\right] \qquad (6)$$

where ϵ is the well depth, R_{m} the distance at the minimum, and α a steepness parameter. Both sets of constants are listed in Table II. The constants were arrived at in a priori fashion in the sense of no data from phosphazenes being used. The Cl···Cl

Table II. Nonbonded Potential Function Parameters[a]

	A	B	C	ϵ	R_m	α
NN	445.5	3.635	2.796	0.0702	3.855	14.015
NP	835.2	3.571	5.854	0.1325	3.921	14.007
NCl	757.9	3.578	5.388	0.1255	3.901	13.958
NF	409.1	4.005	1.479	0.0677	3.485	13.958
PP	1565.8	3.508	12.25	0.2500	3.990	14.000
PCl	1421.0	3.514	11.27	0.2360	3.970	13.954
PF	767.1	3.941	3.096	0.1301	3.535	13.931
ClCl	1289.6	3.521	10.382	0.2245	3.948	13.901
FF	375.8	4.375	0.7829	0.0600	3.200	14.000

[a] The A, B, C parameters are defined in the text in eq 5. The units are the same as in Table I. In the alternative formulation of eq 6, ϵ is the well depth (kcal/mol), R_m is the distance of the minimum (Å), and α the steepness parameter.

function is that determined by Bates and Busing.[30] The N···N function is representative of those reported by Schnepp and coworkers.[31,32] The P···P function was determined by us from the consideration (from the position of phosphorus in the periodic table[11]) that its R_m should be slightly larger (taken to be 3.99 vs. 3.95 Å) and its ϵ more attractive (0.25 vs. 0.22 kcal/mol) than the chlorine function. The F···F function was similarly determined by taking its R_m as slightly larger than that for neon[33] and its ϵ slightly larger. Our function is very similar to one proposed by Bates[34] and found to lead to good results.[35] The unlike atom functions were determined from geometric mean combining rules for A and C and the arithmetic average for B (eq 5). No charges on the atoms were included in the calculations.

Structures, energies, and vibrational frequencies were calculated by minimizing the total conformational energy using algorithms previously described.[10,36] Starting coordinates were obtained from x-ray structures or generated[10] from approximate valence coordinates inspired by inspection of models. Paths between some conformations were investigated by techniques previously used.[37]

Results and Discussion

A major complication of this work is that although both geometries and stabilities (strain energies) are experimentally available, there is no guarantee to which conformer of a given oligomer the stability applies. For example, for the octachloro cyclic tetramer experimental evidence for the existence of four conformers has been given (see above). Our calculations are appropriate to the isolated molecule (vapor phase) and the experimental stabilities are presented on this basis (Figure 3). However, it is not an experimental certainty which of the conformers is the most stable and hence the one to which the experimental strain energy applies. Thus it is one of the goals of the calculations to give a rationalization of the interrelationships among the conformer stabilities. Detailed geometries are available for two puckered conformers in the crystal (S_4 tub[14] and C_i skewed chair[15]) and it is illuminating to compare the calculated (isolated molecule) geometries of these conformers with those in the crystal. We must keep in mind, however, that the crystal forces may well lead to some distortion of the geometry of a given conformer compared to the same conformer as an isolated molecule. It will be important, of course, to calculate a reasonable order of the stabilities of the different conformers of the same compound as well as a quantitatively acceptable value for the most stable one. In the case of the decachloro cyclic pentamer we believe that the crystal conformer is not the most stable for the isolated molecule and have proposed another one as the most stable. However it is nevertheless instructive to compare the calculated geometry (as an isolated molecule) of the crystal conformer with the observed one.

Detailed comparisons of calculated and experimental properties are given below.

Hexachloro and Hexafluoro Cyclic Trimers. The calculated stability of the hexachloro compound is seen in Figure 3 to be adjusted satisfactorily to the experimental. It was found that the nonbonded forces are important in producing the calculated strain energy. Although the formation of the six-membered ring involves considerable PNP valence angle distortion (from 131 to 122° in our parametrization) due to the softness of the bending function, it contributes only ~2 kcal/mol to the strain energy. The rest (~5 kcal/mol) comes from the intra-ring nonbonded interactions, especially the P···N interaction, which is at a distance (3.147 Å) considerably less than its R_m value (Table II).

The calculated vibrational frequencies for the trimers are compared with the experimental in Table III. Since no (valence coordinate) interaction constants (stretch-stretch, stretch-bend, etc.) are included in our force field, we do not hope for extremely close correspondence. However, with a few exceptions the agreement for the perchloro trimer is fairly good. The A_2'' mode calculated to be 367 cm^{-1} is assigned at 540 cm^{-1} and the E'' mode calculated to be 335 cm^{-1} is assigned at 204 cm^{-1}. These modes correspond to out-of-plane motions that are respectively in-phase and out-of-phase around the ring. They both depend heavily on the NPCl bending constant and the torsional barrier. It may well be that introduction of PNCl stretch-bend interactions and reoptimization would greatly reduce this discrepancy. However, a more serious discrepancy exists between the calculated and experimental values of the lowest A_2'' and E'' frequencies and its nature appears to be more fundamental. The symmetry species A_2'' and E'' involve PCl stretching, PCl_2 rocking, and PN out-of-plane motion. We find that there is no set of valence force constants (either related or unrelated to those appropriate to other symmetry species) for these deformations that will come close to fitting all of the vibrations of either species. Inevitably when the higher members of either species are fit, the lowest calculated one falls far below the quoted assigned values (see the added note at the end of this paper for more comment). We suggest the assignments of these frequencies are not correct and the actual fundamentals lie at a much lower frequency. The A_2'' assignment (~190 cm^{-1}) is based on a weak far infrared band. It could easily have another assignment. In Hisatsune's assignment[22] the lowest E'' band is a strong Raman band at 162 cm^{-1}. However Manley and Williams[24] assign this band as the next lowest E'' and assign a band not mentioned by Hisatsune as the lowest one and move the strong Raman band at 177 cm^{-1} to the E' species. It would seem then that the assignments are in doubt and the actual lowest A_2'' and E'' fundamentals could well lie at much lower frequencies and the stronger bands still be accommodated in the assignment. There is in fact a Raman band at 49 cm^{-1} (that Hisatsune assigns[22] as a difference band) that could well be the lowest E'' band and would

Table III. Calculated and Experimental Vibrational Frequencies (cm^{-1}) of Hexachlorocyclotriphosphaazene

Symmetry D_{3h}	Species ν_i	Exptl[a,b] (1)	(2)	(3)	(4)	Calcd
A_1'	ν_1	$\underline{783}$	785	$\underline{785}/\underline{670}$	$\underline{785}/\underline{671}$	804
	ν_2	$\underline{668}$	671	$\underline{670}/\underline{575}$	$\underline{671}/\underline{785}$	637
	ν_3	$\underline{365}$	365	$\underline{365}$	$\underline{365}$	294
	ν_4	304	308	$\underline{100}$	76?	178
A_2'	ν_5		1370	875?		1252
	ν_6					267
E'	ν_7	$\underline{1210}$	1226	$\underline{1226}$	$\underline{1310}/\underline{1218}$	1209
	ν_8	$\underline{1190}$	877	$\underline{1202}/875$	$\underline{336}$	913
	ν_9	$\underline{524}$	533	$\underline{533}$		540
	ν_{10}	$\underline{338}$	336	$\underline{336}$	$\underline{527}$	281
	ν_{11}	220	216	(150)		221
	ν_{12}	140	176			119
A_1''	ν_{13}					109
A_2''	ν_{14}	$\underline{598}$	601	$\underline{619}$		633
	ν_{15}	540	544	$\underline{552}$	$\underline{612}$	367
	ν_{16}	189	192			33
E''	ν_{17}	576	582	575/610	885	606
	ν_{18}	$\underline{204}$	206	$\underline{210}$	$\underline{173}$	335
	ν_{19}	$\underline{177}$	162	$\underline{173}$	$\underline{210}$	145
	ν_{20}	$\underline{162}$	131	$\underline{162}$	$\underline{162}$ (49)[c]	36

[a] Underlined frequencies are of "strong" or "very strong" intensity in IR spectrum and/or of intensity ≥2 in Raman spectrum. [b] (1) ref 22; (2) ref 24; (3) ref 21; and (4) ref 20. [c] There is a Raman band at 49 cm^{-1} (ref 22) that we propose may be the lowest E″ mode.

Table IV. Calculated and Experimental Vibrational Frequencies (cm^{-1}) of Hexafluorocyclotriphosphazene

Symmetry D_{3h}	Species ν_i	Experimental[a,b] (1)	(2)	(3)	Calcd
A_1'	ν_1	$\underline{743}$	681	$689/\underline{570}$	773
	ν_2	567	567	$\underline{570}/689$	536
	ν_3	952	742	$\underline{743}$	1007
	ν_4	470	633	$\underline{311}$	317
A_2'	ν_5				1256
	ν_6				494
E'	ν_7	$\underline{1305}$	$\underline{1300}$	$\underline{1287}$	1240
	ν_8	$\underline{975}$	1007	1338?	1022
	ν_9	$\underline{516}$	$\underline{511}$		522
	ν_{10}	$\underline{860}$	$\underline{865}$	$\underline{862}$	844
	ν_{11}	$\underline{465}$	$\underline{464}$	$\underline{465}$	335
	ν_{12}	336	339		248
A_1''	ν_{13}				278
A_2''	ν_{14}	$\underline{887}$	$\underline{970}$	$\underline{963}$	995
	ν_{15}	534		$\underline{510}$	514
	ν_{16}	372			59
E''	ν_{17}		950	962?	986
	ν_{18}	280	$\underline{307}$		496
	ν_{19}	309	$\underline{278}$	$\underline{282}$	288
	ν_{20}		251		60

[a] Underlined frequencies are of "strong" or "very strong" intensity in IR spectrum and/or of intensity ≥2 in Raman spectrum. [b] (1) ref 20; (2) ref 27; and (3) ref 28.

Table V. Calculated and Observed (x-ray) Structures of Cyclic Trimers

	Hexachloro Calcd	Hexachloro Expt[a]	Hexafluoro Calcd	Hexafluoro Expt[b]
	Torsional Angles, deg			
1 2 3 4	0.0	−5.6	0.0	−1.4
2 3 4 5	0.0	7.9	0.0	1.4
3 4 5 6	0.0	−7.9	0.0	−0.3
4 5 6 1	0.0	5.6	0.0	−0.8
5 6 1 2	0.0	−3.3	0.0	0.8
6 1 2 3	0.0	3.3	0.0	0.3
	PNP Valence Angles,[c] deg			
1 2 3	121.3	121.5	121.1	121.1
3 4 5	121.3	121.2	121.1	121.1
5 6 1	121.3	121.5	121.1	119.6
	NPN Valence Angles,[c] deg			
2 3 4	118.7	118.3	118.9	119.4
4 5 6	118.7	118.5	118.9	119.4
6 1 2	118.7	118.5	118.9	119.4
	P N bond length,[d] Å			
	1.574	1.575	1.574	1.546-1.572

[a] Reference 12. [b] Reference 13. [c] The valence angles involving the halogen substituents undergo small deviations from the relaxed values of Table I, but are not shown in the interests of brevity. [d] The PCl, PF bond lengths are very close to the relaxed values of Table I.

agree well with our calculated value.

The calculated frequencies of the hexafluoro cyclic trimer are compared with several experimental assignments in Table IV. It appears that the principal features of the spectrum are satisfactorily reproduced by the calculations. Again we predict the lowest A_2'' and E″ modes to be very low frequencies, but there is little experimental information bearing on this.

The calculated geometries of the perchloro and perfluoro cyclic trimers are compared with the experimental in Table V. The force field satisfactorily reproduces the PNP and NPN valence angles. The experimental structure is very slightly puckered, while the calculated one is not. However, in view of the high degree of out-of-plane flexibility suggested by our calculated frequencies, the puckering could easily be produced by crystal packing.

Octachloro and Octafluoro Cyclic Tetramers. The energetic interrelation among four conformers of the perchloro tetramer resulting from our calculations is shown in Figure 1. We find that there is essentially free pseudorotation of the ring between the tub and boat forms and that these forms are the most stable. The skewed chair[15] is apparently the more stable crystal form (compared to the tub[14]). However, we attribute this to crystal packing stabilization. The tub would appear to provide some intramolecular shielding of possible intermolecular interactions compared to the chair.

Our force field predicts that the planar (D_{4h}) conformer is

Table VI. Calculated and Observed (x-ray) Structures of Cyclic Tetramers[a]

	Octachloro				Octafluoro	
	S_4 tub		C_i chair		D_{4h} planar	
	Calcd	Expt[b]	Calcd	Expt[c]	Calcd	Expt[d]
			Torsional Angles, deg			
1 2 3 4	−2.8	−15.6	17.7	19.8	0.0[e]	5.9
2 3 4 5	(54.9)	57.3	44.6	45.3	0.0	−6.4
3 4 5 6	2.8	15.6	(−75.5)	−75.8	0.0	3.8
4 5 6 7	(−54.9)	−57.3	59.5	59.4	0.0	2.8
5 6 7 8	−2.8	−15.6	−17.9	−19.8	0.0	−5.9
6 7 8 1	(54.9)	57.3	−44.5	−45.3	0.0	6.4
7 8 1 2	2.8	15.6	(75.5)	75.8	0.0	−3.8
8 1 2 3	(−54.9)	−57.3	−59.4	−59.4	0.0	−2.8
			PNP Valence Angles,[f] deg			
1 2 3	132.6	131.3	133.3	133.6	146.6	147.1
3 4 5	132.6	131.3	135.6	137.5	146.6	147.1
5 6 7	132.6	131.3	133.3	133.6	146.6	147.1
7 8 1	132.6	131.3	135.6	137.5	146.6	147.1
			NPN Valence Angles,[f] deg			
2 3 4	121.4	121.2	121.8	121.7	123.3	123.2
4 5 6	121.4	121.2	121.6	119.4	123.3	122.3
6 7 8	121.4	121.2	121.8	121.7	123.3	123.2
8 1 2	121.4	121.2	121.6	119.4	123.3	122.3
			PN bond length,[g] Å			
	1.570	1.570	1.570	1.559	1.570	1.49–1.52

[a] The torsional angle values enclosed in parentheses indicate that the angle was constrained at that value in the energy minimization calculation. The rings are so flexible that at minimum energy they do not have a conformation of fixed geometry. They have to be constrained for comparison with the x-ray structures. [b] Reference 14. [c] Reference 15. [d] Reference 16. [e] The calculated structure converges to D_{4h} planar symmetry when started from a planar trial structure. However, this structure has two calculated vibrational frequencies that are nearly zero or even imaginary, indicating that the planar structure is not a local minimum, but a very broad saddle point. When started from the x-ray structure coordinates the calculated structure converges to a slightly puckered ring with energy almost imperceptibly lower than the planar one, but with all positive vibrational frequencies. [f] The valence angles involving the halogen substituents undergo some deviation from the relaxed values of Table I, but are not shown in the interests of brevity. [g] The PCl, PF bond lengths are very close to the relaxed values of Table I.

not as stable as the tub–boat. Hisatsune,[25] based on the observation that the 890-cm^{-1} band disappeared in the vapor and other simplifications in the spectrum, proposed that the planar form is the observed form there (and therefore the most stable conformer). Before rationalizing this observation we must first make some asides. In our parametrization we could force the tub–boat to be of higher energy than the planar conformation by increasing the rotational barrier. However, when this is done the geometry of the tub becomes in progressively worse agreement with the x-ray structure in that the ring flattens out as the barrier increases. Furthermore, the chair becomes unreasonably high in energy compared to the tub. In fact, the x-ray structures are probably best accommodated by a barrier that is as low as possible. However, lowering the barrier below our adopted value makes the puckered tetramer too stable, and the strain energy disappears in contradiction to experiment (Figure 3). As an alternative one might suppose that the observed strain energy is due to a cis–trans energy difference (rather than a barrier), there being more nearly cis bonds in the rings than in the open chain linear polymer. Indeed we have adjusted the strain energies for agreement with experiment by imposing a small stability of trans over cis (0.3 kcal/mol). However, lowering the barrier below our adopted value and increasing the cis–trans difference to bring agreement in the strain energy of the cyclic tetramer rapidly pushes the strain energy of the cyclic trimer too high, out of the observed range.

Returning to the question of the stability of the planar conformation of the cyclic tetramer, one would suppose that if it were the most stable conformer, then it would be observed in the crystal (since it would be expected to pack favorably), liquid, and vapor. It is the observed crystal conformation in the perfluoro tetramer.[16] However the high symmetry is lost in the liquid.[20,27] This is what one would expect if the planar molecule were favored by crystal packing, but not the most stable isolated molecule conformation. Thus we believe that our parametrization, which places the planar form as of comparable stability to other conformers, but not at the lowest energy, is quite reasonable. To have the planar molecule of comparable energy to the puckered forms places a further constraint on the value of the rotational barrier. Too low a barrier value would result in the planar form being far too high in energy (since it contains valence angle strain) compared to the puckered forms observed in crystals.

We believe that the simplification in the vibrational spectrum in the vapor phase can be rationalized on the following grounds. The pseudorotation of the D_{2d} boat–S_4 tub system results in atoms becoming equivalent with respect to their positions above and below the reflection plane of the S_4 axis. The situation is closely analogous to the pseudorotation of the ring puckering in cyclopentane.[38] The in-plane vibrations of the latter obey D_{5h} selection rules in spite of the considerable lack of planarity.[38] In our case, we may reasonably expect the in-plane vibrations in the pseudorotating puckered molecule to obey D_{4h} selection rules. We thus interpret the changes in the vapor spectrum as due to the onset of pseudorotation in the vapor that is inhibited in the liquid and solid states.

The calculated structures of cyclic tetramers are compared with x-ray structures in Table VI. In order to make the comparison the pseudorotation of the tub–boat had to be "frozen" to give the proper symmetry. This was done by constraining some of the torsional angles to the fixed values indicated in the table. The constraint was supplied by torsional potentials with artificially high barriers and false minima at the desired values.[37] Similarly, the unconstrained skew chair was too flexible to minimize to a definite conformation and had to be

Table VII. Calculated and Observed (x-ray) Structures of Decachlorocyclopentaphosphazene

	Indented ring (crystal)		C_2 form
	Calcd[a]	Expt[b]	calcd
	Torsional Angles, deg		
1 2 3 4	−172.4	176.0	−66.3
2 3 4 5	2.4	6.6	−9.0
3 4 5 6	−2.6	−19.1	−9.0
4 5 6 7	172.1	166.3	−66.3
5 6 7 8	−177.5	−156.5	137.1
6 7 8 9	(36.0)	35.5	−13.7
7 8 9 10	(−58.6)	−57.1	−21.3
8 9 10 1	(58.6)	59.2	−21.4
9 10 1 2	(−36.0)	−38.7	−13.7
10 1 2 3	178.0	−168.1	137.1
	PNP Valence Angles,[c] deg		
1 2 3	152.8	158.9	136.0
3 4 5	125.6	133.6	132.3
5 6 7	152.8	157.2	136.0
7 8 9	139.4	149.8	138.2
9 10 1	139.4	143.3	138.2
	NPN Valence Angles,[c] deg		
2 3 4	118.7	119.0	121.1
4 5 6	118.7	116.0	121.1
6 7 8	120.4	117.3	121.5
8 9 10	123.7	121.2	123.1
10 1 2	120.4	118.3	121.5
	PN Bond Lengths,[d] Å		
	1.567–1.572	1.487–1.552	1.571

[a] The parentheses indicate that the torsional angle was constrained at that value in the energy minimization. [b] Reference 17. [c] The valence angles involving the halogen substituents undergo some deviation from the relaxed values of Table I, but are not shown in the interests of brevity. [d] The PCl, PF bond lengths are very close to the relaxed values of Table I.

Table VIII. Calculated Structures of Linear Perhalo Tetramers

	$P(NPX_2)_4N$			
	Perchloro,	Perfluoro		
	calcd	Calcd[a]	Calcd[b]	Expt[c]
	Torsional Angles, deg			
1 2 3 4	0.0	0.0	0.0	
2 3 4 5	180.0	180.0	180.0	
3 4 5 6	0.0	0.0	0.0	0
4 5 6 7	180.0	180.0	180.0	180
5 6 7 8	0.0	0.0	0.0	0
6 7 8 9	180.0	180.0	180.0	
7 8 9 10	0.0	0.0	0.0	
	PNP Valence Angles, deg			
1 2 3	132.4	132.5	133.5	
3 4 5	134.2	132.8	134.1	136
5 6 7	134.7	132.9	134.2	136
7 8 9	136.0	133.4	134.8	
	NPN Valence Angles, deg			
2 3 4	121.1	121.3	121.4	
4 5 6	120.9	121.2	121.3	119
6 7 8	120.9	121.2	121.3	119
8 9 10	121.6	121.4	121.5	
	PN Bond Lengths, Å			
	1.570–1.572	1.570–1.571	1.521–1.522	1.52

[a] Calculated using the "standard" relaxed PN bond distance of 1.57 Å (Table I). [b] Calculated using a shorter relaxed PN bond length = 1.52 Å, which leads to the same PN length as experimentally found in the high polymer (ref 8). [c] Structural parameters of the linear perfluoro high polymer determined by x-ray diffraction (ref 8).

constrained. In general the calculated structures agree rather well with the observed. The range of PNP valence angles is reproduced satisfactorily, including the predicting of a "splitting" to two values in the skew chair.

Decachloro Cyclic Pentamer. The cyclic pentamer is also very flexible. In order to produce a conformer similar to that observed in the crystal it was again necessary to constrain some of the torsional angles. The calculated geometry is compared with the experimental one in Table VII. The agreement is not as good as for the trimers and tetramers, but a reasonable representation of the structure is obtained. We also found a more stable conformer without the extreme valence angle deformations of the crystal conformer (Figure 2). It has a C_2 axis, whereas the indented form has a symmetry plane in our calculation (and only an approximate one in the x-ray structure). The stability of the C_2 conformer is in good agreement with the experimental isolated molecule strain energy (Figure 3). Its geometry is also listed in Table VII. The crystal conformer is a considerably more planar molecule than the C_2 form as judged from the deviations of the atom coordinates from one of the coordinate planes when the coordinates are referred to principal axes. It would appear that its existence is determined by achieving maximum exposure (i.e., planarity) to neighboring molecules in the crystal.

Linear Oligomers. Calculations were performed on the perchloro linear (cis–trans) dimer, trimer, and tetramer in order to establish a conformational energy increment for the $-N{=}PCl_2-$ group (−1.85 kcal/mol). This increment multiplied by the mer number was subtracted from the conformational energies of the cyclic *n*-mers to provide calculated strain energies.

The calculated geometries of the perchloro and perfluoro tetramers are shown in Table VIII and for the latter compared with the observed one. Unfortunately the accuracy of the experimental structure of the perchloro polymer is not high enough to be diagnostic. In our force field we have adopted just one value for the relaxed PN bond length and the rationale for this is discussed below. However the experimentally determined PN length in the perfluoro linear high polymer is significantly shorter than that resulting from our "standard" value. Consequently, we have also calculated the structure using a shorter relaxed PN length. This second structure has slightly larger PNP valence angles due to increased P···N nonbonded repulsions than the first calculation. The perfluoro structure has slightly smaller PNP valence angles than the perchloro one (for the same relaxed PN length) due to decreased nonbonded repulsions (fluorine vs. chlorine). The second perfluoro structure is in quite good agreement with the experimental. This is especially true if one hypothesizes that the NPN valence angle is actually likely to be nearer the calculated 121° value, which in turn would lead to a PNP angle near 134° for the same experimental repeat distance (4.86 Å).

PN Bond Lengths. In our force field (Table I) we have used a fixed value of the relaxed PN bond distance in all compounds independent of any geometric factors and substituents. There are, however, significant variations in the observed (x-ray) PN bond lengths that if experimentally correct cannot be accounted for by ring strain or nonbonded interactions. Schlueter and Jacobsen[17] proposed a correlation of decreasing bond length with increasing PNP valence angle. However Zoer and Wagner,[39] reviewing the evidence along with their newly determined structures of the perbromo cyclic trimer and tetramer (where in both compounds they find a PN length of 1.575 Å), point out that such a correlation does not appear to be general. From our point of view it would be a relatively simple matter to build such a correlation into the force field. However, we tend to agree with Zoer and Wagner that the experimental evidence at present is not clear. It is not clear either whether there is a substituent effect on PN bond lengths. The hexafluoro, chloro, and bromo cyclic trimers all have roughly comparable PN distances (1.57 ± 0.01 Å). However, the perfluoro cyclic tetramer and the linear high polymer experimentally both have significantly shorter PN distances (~1.52 Å). The necessarily lower accuracy obtainable in the high polymer structure determination, however, makes it difficult to decide how much weight to give the apparently shorter distance found there. Consequently, we have presented our force field with just one relaxed PN distance. However, it is a trivial matter to adjust it to other values if desired. As indicated above we have made calculations on the linear perfluoro oligomers with two values of the relaxed PN distance.

Summary

The geometries, stabilities, and vibrational frequencies of the perhalo oligomers considered here seem to be, on the whole, satisfactorily reproduced. This would indicate that the phosphazenes behave as systems in which the bond properties are independent of the molecular size and geometry. It thus appears that they are promising as a class of molecules whose properties may be investigated by means of conformational energy calculations. The main features of the conformational model are a soft PNP bending function and a low but finite barrier to rotation about the PN bond. The value of the barrier is largely determined by experimental strain energies of the cyclic oligomers and is bounded on the high side by the geometries of the cyclic tetramers and on the low side by the fact that planar and puckered conformers are energetically competitive.

Added Note. One of the reviewers has made the reasonable suggestion that perhaps the lack of agreement between our calculated lowest E″ and A$_2$″ frequencies and the literature assignments in the cyclic trimers is due to anharmonic effects in the effective ring puckering potential. Since our frequencies are calculated in the harmonic approximation and ring puckering potentials are often highly anharmonic[40,41] this point deserves comment. We have approached this question from two points of view. The first one is an analytical one based on a slightly simplified model. In the A$_2$″ species, numbering the atoms of a NPCl$_2$ group P = 1, N = 2, Cl = 3,3′, the following Cartesian displacements result (Z = out-of-plane, X = in-plane along ring (bisector)): Z_1, Z_2, $Z_3 = Z_{3'}$, $X_3 = -X_{3'}$. The potential energy for ring puckering in the approximation of equal ring valence angles and force constants and neglecting the cis–trans energy difference and valence angle anharmonicity is

$$V = 6[V_2/2(1 - \cos 2\phi) + (k_\theta/2)(\theta - \Theta_0)^2] \qquad (7)$$

where θ is the PNP, NPN valence angle.

Defining $\delta = (Z_2 - Z_1)/R$, R = PN bond length, eq 7 can be expanded about $\phi = 0$, $\theta = 2\pi/3$ as

$$V = 6[(24V_2 + \sqrt{3}(\Theta_0 - (2\pi/3)k_\theta)\delta^2 + {}^3\!/_2 k_\theta\delta^4 + \cdots] \qquad (8)$$

A realistic estimate of an upper bound on the effect of the anharmonic (δ^4) term in this effective ring puckering potential on the lowest A$_2$″ fundamental can be made by considering the substituents to be rigidly fixed to the ring. In that case $X_3 = (2c/R)(Z_2 - Z_1)$, $Z_3 = (-2a/R)(Z_2 - Z_1)$, where a and c are the in-plane and out-of-plane components, respectively, of the PCl bond distance. The kinetic energy is then $T = {}^1\!/_2\mu\dot{\delta}^2$ where

$$\mu = {}^3\!/_2\left[M_1 + M_2\alpha^2 + 2M_3\left(\left(\frac{2a}{R}\right)^2 + \left(\frac{2c}{R}\right)^2\right)(1 + \alpha)^2\right]\frac{R^2}{(1 + \alpha)^2} \qquad (9)$$

and

$$\alpha = \frac{2M_3(2a/R) + M_1}{M_2 - 2M_3(2a/R)}$$

We further point out that since harmonic terms necessarily predict a fundamental far below 200 cm^{-1} when the upper members of the A$_2$″ species are fit, any fit to the lowest frequency at ~200 cm^{-1} would have to come almost entirely through the dominance of the δ^4 term in eq 8. Thus we investigate the eigenvalues of the potential, $V = b\delta^4$ ($b = 9k_\theta$), with effective mass, μ. According to Bell[42] the fundamental frequency resulting from this potential is

$$\nu = \frac{2.739}{4\pi}\left(\frac{bh}{\pi\mu^2}\right)^{1/3} \qquad (10)$$

We evaluate μ (eq 9) 5550 Awu Å^2 and for $k_\theta \sim 1 \times 10^{-11}$ erg/molecule we calculate the fundamental at ~4 cm^{-1}. Thus physically realistic values of b lead us to expect that anharmonicity will give at most a small correction to harmonically calculated frequencies. Larger physically unrealistic values of b leading formally to larger calculated values of the puckering frequency also suffer from the catastrophe of requiring physically unrealistic vibrational amplitudes.

As a second approach we have also numerically generated an effective potential by minimizing the total conformational energy with the ring torsional angles constrained at increasing values corresponding to increasing puckering. Force constants for the substituents from Table I were used rather than the rigid substituent approximation. There is no appreciable anharmonicity out to increases in energy with puckering larger than 190 cm^{-1}. Furthermore, the effective mass generated is comparable to that calculated by means of eq 9, indicating again that even with unrealistically large anharmonic constants the calculated fundamental is far below 190 cm^{-1}. Therefore, we feel confident that anharmonicity associated ring puckering would contribute only small corrections to harmonically calculated frequencies and does not alter the conclusion that the lowest A$_2$″ (and E″) frequencies must lie far below 190 cm^{-1}.

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Conformational Analysis. 126. The Conformations and Electronic Spectra of Small Nonplanar Polyenes[1,2]

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Abstract: Accurate geometries for a number of small polyenes were obtained by molecular mechanics calculations. The electronic spectra of these molecules were then calculated using the standard VESCF-MO method, including doubly excited configurations in the configuration interaction treatment. Nonplanar systems can now be dealt with in a straightforward way, and the results obtained are satisfactory.

Earlier studies have shown that the variable electronegativity self-consistent field method, when both singly excited and doubly excited configurations were included in the configuration interaction treatment, was capable of giving reasonably accurate predictions of the electronic spectra of planar polyenes.[3,4] The earlier calculations were essentially limited to planar systems, because for nonplanar molecules, there was no good general method then available for determining the degree of nonplanarity, upon which the electronic spectrum is highly dependent. The molecular mechanics method now furnishes such a procedure,[5,6] and has been employed herein. The spectroscopic calculations follow the scheme and parametrization discussed earlier.[3] Depending on the particular geometric features of a given polyene it may be either planar or twisted by any amount up to 90° about one or more of the formally single bonds in the system. In the present work we have examined a number of typical molecules of varying degrees of nonplanarity. In addition, many polyenes are expected to be conformational mixtures. The molecular mechanics procedure now also gives us a method for estimating the energy differences between conformations, and hence it allows us to compute the effect of the conformational Boltzmann distribution on the expected electronic spectrum.

Of course, when a polyene has a nonplanar geometry, the σ–π separation is no longer strictly valid. It is, however, usually quite a good approximation, as shown by the agreement of calculations with experiment.

The most extensive systematic calculation of the electronic spectra of geometric isomers (including conformers) of small molecules was that by Simmons,[7] which was concerned with 1,3,5-hexatriene and 1,3,5,7-octatetraene. He had to assume "standard geometries" and planar molecules in his calculations. In addition, he neglected the effect of solvent on the transition energies. By suitable parametrization, solvent effects can be implicitly allowed for. However, a better procedure is to explicitly include solvation, which we will do here.

Results and Discussion

The exact structure of each conformer (minimum energy structure) was obtained by employing the molecular mechanics method mentioned above. A VESCF-CI treatment including all singly and doubly excited configurations[3,4] was then carried out to obtain the transition energies and oscillator strengths. The calculated spectra are summarized in Table I and compared with the available experimental data. Bond lengths and bond angles are omitted from Table I. They vary within small ranges and have relatively little effect on spectral changes. For molecules with nonplanar carbon skeletons, the dihedral angles ω of the relevant carbon-carbon bonds are given with the structural formula.[16]

A preliminary study showed several important points. First, there were always two transitions very close in energy at the longest wavelength, one strongly allowed, one forbidden, for systems with C_2 symmetry. Destroying the symmetry of the molecule led to mixing of these transitions, the oscillator strengths becoming weaker and stronger, respectively. This near degeneracy of the long wavelength $\pi \rightarrow \pi^*$ transitions has been long known with α,β-unsaturated ketones,[8] and is correctly calculated by the current method employing doubly excited configurations. Experimentally, the second transition has too low an oscillator strength to be detectable in the ultraviolet spectrum in the presence of the nearby intense band. The two transitions often show Cotton effect curves of opposite signs, however, and are readily discernible in optical rotatory dispersion or circular dichroism spectra. We find calculationally a similar near degeneracy of the long wavelength transitions with polyenes. It should be noted that calculations which do not include doubly excited configurations in the