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Solution Conformations of Unconstrained Eight-Membered 1,5-Heterocycles Containing Sulfur and Phosphorus

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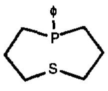
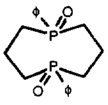
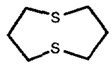
Abstract: *The conformational analysis of three unconstrained eight-membered heterocycles (1, 5- dithiacyclooctane (1,5-DTCO), 1-phenyl-1-phospha-5-thiacyclooctane, and trans-1, 5-diphenyl-1,5-diphosphacyclooctane 1,5-dioxide) has been carried out. The relative energies of all possible conformations were calculated and their appropriately weighted contributions yielded good simulations of the ^{1}H NMR spectra of these compounds.* © 1997 Elsevier Science Ltd.

In the course of our studies of the synthesis and reactivity of unconstrained eight membered heterocycles[1], e.g. 1-phenyl-1-phospha-5-thiacyclooctane[2,3], *trans*-1,5-diphenyl-1, 5-diphosphacyclooctane 1, 5-dioxide[2], and 1, 5-dithiacyclooctane (1, 5-DTCO)[4-7], we noticed that the ^{1}H NMR spectra of these ring systems displayed a pattern which suggested that more than one conformation had to be present in solution.







Crystalline *trans*-1, 5-diphenyl-1,5-diphosphacyclooctane 1,5-dioxide and 1-phenyl-1-phospha-5-thiacyclooctane each exhibit asymmetric boat-chair conformations with equatorial phenyl rings and pseudo-axial oxygen atoms[2,3]. Crystalline complexes containing 1,5-DTCO show both boat-chair and chair-chair ring conformations[8], but nothing has yet been published concerning the conformational behavior of unconstrained, eight-membered 1,5-heterocycles in solution. To this end, we have now estimated the relative energies of the accessible conformations of the three molecules of interest, and then using both Boltzmann factor and statistical weighting calculated proton-proton vicinal coupling constants that agree well with the experimental ones.

Spectral Data

Routine proton and carbon-13 {^{1}H} NMR spectra were run on either Nicolet NT-360 or General Electric QE-300 spectrometers. Chemical shift values are given in ppm downfield from internal tetramethylsilane. All ^{31}P-decoupled ^{1}H spectra, including selective proton irradiation experiments and all two-dimensional experiments, were recorded on a Nicolet NT-500 FT spectrometer using a wide band probe (possessing wideband, proton, and deuterium-locking channels) with an external frequency synthesizer set to the exact phosphorus resonance frequency of each sample. Approximately 44 dBM (10 watts) of Rf power was then run into the wideband channel (tuned to 202.4 MHz) to effect phosphorus decoupling.

Phosphorus decoupled, two-dimensional correlated ^{1}H NMR (COSY) spectra were obtained by applying the conventional sequence: $(\pi/2)$ - (t_1) - $(\pi/2)$ - (FID, t_2). The solutions for the COSY experiments were typically 0.5M (~7% by weight) in $CDCl_3$ for the heterocycle 1-phenyl-1-phospha-5-thiacyclooctane and 0.2M for *trans*-1, 5- diphenyl-1,5-diphosphacyclooctane 1,5-dioxide. For 1-phenyl-1-phospha-5-thiacyclooctane, the spectral widths were 1400 Hz in the F_2 and F_1 dimensions, allowing a digital resolution of 2.7 Hz per point (the aromatic resonances were excluded from the spectral window). For *trans*-1, 5- diphenyl-1,5-

diphosphacyclooctane 1,5-dioxide, the spectral widths were 1200 Hz in F_2 and F_1, with a digital resolution of 1.2 Hz per point. The number of data points in F_2 was 1024 for all COSY experiments and 128 increments were recorded. Before Fourier transformation, the data were multiplied by a sine apodization function to reduce tailing of peaks in the processed 2D NMR spectra. Zero filling was applied twice in the F_1 dimension. After one dummy scan, 48 transients were collected for 1-phenyl-1-phospha-5-thiacyclooctane and *trans*-1, 5-diphenyl-1,5-diphosphacyclooctane 1,5-dioxide in each t_1 increment. The recycle delay time was 4.6 s in all cases.

General Conformational Considerations

The conformations of small or medium rings may be described using either the pictorial language introduced by Hendrickson[9], or an alternative approach introduced by Dale[10] which focuses on the sequential behavior of the ring torsion angles.

In Dale's terminology, a "corner" is a ring atom at which two ring-bond torsion angles of the same sign meet. An eight-membered ring in a crown conformation has no corners. The Hendrickson "twist-chair-chair" conformation of an eight-membered ring heterocycle is crown-like, with torsion angle signs that alternate around the ring with successive magnitudes of approximately 60, 85, 115, 85, 60, 85, 115 and 85°. The same molecule in a "boat-chair" conformation has two corners that are two bonds apart, while a "twist-boat-chair" conformation has two corners that are three bonds apart the short way. Ring conformational changes entail either creating corners or moving them around the ring.

On this basis, it is not difficult to enumerate the possible conformations of a 1,5-diheterocyclooctane molecule. In principle, two "crown" structures are possible if the molecule has different entities in those positions since heteroatom-1 could be flanked either by 60° and 85° or 85° and 115° torsion angles. In practice, their relative energies could be such that at reasonable temperatures one of them could be ignored for practical purposes.

From an energy standpoint, molecules of the type of interest here can exhibit at most five unique boat-chair conformations. The atom **between** the "corner" atoms can start out in the 1-position and progress around the ring (either clockwise or counterclockwise) by an appropriate sequence of gauche torsion angle changes until it reaches the 5-position. Further steps in the same direction will then produce enantiomers of preceding ones. The existence of enantiomers must be recognized to do the overall counting correctly, but their energies do not have to be recalculated. Similar considerations show that there are four possible energetically distinct twist-boat-chairs. With a 1,5 di-heterocyclooctane there is one more conformation that could also be a local energy minimum--namely, one with "corners" at the two middle carbon atoms on opposite sides of the ring (four bonds apart).

To summarize: if only one crown structure is accessible, the conformational potential energy surface of one of these molecules will involve a total of eleven distinctive structures if the entities in the 1 and 5 positions are different from each other, and their own local conformations are invariant. This last statement recognizes, e.g., that a molecule which can have either an axial or an equatorial phenyl substituent on the heteroatom in the 1-position with no possibility of their interconversion, would yield two potential energy surfaces having the same number of local energy minima as each other, but with different energies for the pairs of ring conformers with different orientations of the phenyl group.

The Conformations of 5-phenyl-1-thia-5-phosphacyclooctane

The ideas presented in the preceding paragraphs were used to construct the conformational potential energy surface for 5-phenyl-1-thia-5-phosphacyclooctane. The MMX molecular mechanics routine contained in the program PCMODEL, Version 4[11], was used to estimate the relative energies of the various conformers. The results of these calculations are presented in Figure 1. The calculated global energy minimum for this molecule, shown as Conformation I in Fig. 1, is a twist-chair-chair structure with the phenyl group on phosphorus equatorial. The calculated 4567 torsion angle is +114°. Without exception, the structures with the phenyl group axial were at least 2 kcal/mole higher energy than their equatorial counterparts (cf. Conformations VIII and XII in Fig. 1.)

An attempt to create a corner by driving torsion angle 6781 of Conformation I from ~+60° to ~-60° carried the molecule over a 10 kcal/mol energy barrier to a boat-chair conformer in which both the 5678 and 6781 torsion angles became inverted, creating corners at atoms 6 and 8. In Figure 1 "corners" are denoted by x's at or near where a ring atom would be. By coincidence, the calculated energy of this conformation, labeled II in Figure 1, is the same as that of Conformation I. The energy barrier we find between the crown conformation and the family of boat-chair conformations is consistent with barriers in the 8-10 kcal/mol range reported by Anet[12] as having been found in other eight-membered ring systems.

The remaining features of Figure 1 have straightforward interpretations. The four-digit numbers are the atom labels of a torsion angle being driven, and the decimal numbers are the energies of either the conformation in question if they are inside a structure or of the transition state between conformations if they are beside a directional arrow. *All energies are referred to the same common zero.* Thus the figure of 4.8 kcal/mol beside the arrow joining Conformations III and IV implies that only a 1.05 kcal activation barrier has to be surmounted to convert III into IV.

The three conformations with mirror planes (X, XI and VI) have such high relative energies that their equilibrium populations will be negligible around room temperature, but they are nonetheless present as transient intermediates. In any one of these symmetrical conformations three geminal pairs of chemically and magnetically distinct protons will be found in each half (left or right on the figure) of the molecule. Thus, if the molecule existed predominantly in one of these conformations, the high resolution PMR spectrum would have six distinct multiplets with each of them integrating to two protons.

Although the low-energy conformers of this molecule have no symmetry elements, it remains true that there will be six well-defined "kinds" of protons on a time-averaged basis. A molecule transiting Conformation X of Fig. 1 can exit it either via the pathway 6781 yielding corners at atoms 2 and 7, or by the energetically equivalent 4321 route that puts corners at atoms 3 and 8. On the average, therefore, the protons bonded to carbons 2 and 8 will experience identical environments in a pairwise fashion. Similar arguments can be offered involving structures VI for sites 3, 7 and XI for sites 4, 6. The fact that the enantiomer of any unsymmetrical conformation is readily accessible insures the pairwise average equivalence of the protons on the two "sides" of the molecule.

This observation is quite important because operationally one can then label the protons in one of the symmetrical structures and keep track of pseudo-symmetry related pairs as the molecule roams through its accessible conformations. In each such conformation a given proton will couple both to its geminal partner and to the vicinal pair on any adjacent methylene group. The experimental PMR spectrum can then be explained by assuming that the observed coupling constants are statistically and energetically weighted averages of the appropriate coupling constants in the contributing conformations.

The PMR Spectrum of 5-phenyl-1-thia-5-phosphacyclooctane

Figure 2 presents three depictions of the 500 MHz PMR spectrum of 5-phenyl-1-thia-5-phosphacyclooctane in the aliphatic region. Curve (a) is the experimental spectrum. Curve (b) is the experimental phosphorus-decoupled spectrum, and curve (c) is a theoretical simulation of curve (b) made with the program PMR[13] using the parameters given in Table I *(vide infra).*

A comparison of spectra (a) and (b) suggests that the spectral features with chemical shifts less than 2.4 ppm arise from protons that are either directly bonded to or are coupled to protons on a methylene group next to phosphorus. Decoupling the phosphorus only minimally affected the two multiplets with chemical shifts greater than 2.4 ppm, so they most likely arise from two protons on a methylene group next to sulfur. The experimental COSY plot confirmed that the protons in question are geminal.

Since the two downfield multiplets each consist of eight essentially equally spaced lines, these geminal protons must have virtually the same set of coupling constants to the two protons in a vicinal methylene group.

It is clear that the broad spectral feature between about 2.0 and 2.25 ppm must arise from three different protons. The COSY plot suggested that the protons on the carbon next to sulfur (protons A and B) couple to the two upfield protons in the broad 2.0-2.25 ppm multiplex (protons D and E). All the quantitative spectral analyses reported here were done with the program LAOCN3[14].

Absent any other information about the molecule, there would be two equally valid simulations of the spectra arising from protons A and B. In both cases the chemical shifts of the four protons and the AB geminal coupling constant are given by δ_A= 2.834, δ_B = 2.590, δ_D = 2.108, δ_E = 2.056, J_{AB}=-14.94, but the two sets of coupling constants {J_{AD}=8.28, J_{AE}=3.15, J_{BD}=3.51, J_{BE}=8.35 Hz} or {J_{AD}=3.15, J_{AE}=8.28, J_{BD}=8.35, J_{BE}=3.51 Hz} yield identical calculated spectra in the A and B regions because the resonances of protons D and E are so far removed from those of A and B.

Peak F, at δ = 1.883 in Fig. 2 also has 8 components, implying coupling to 3 other protons (one geminal and two on an adjacent methylene), so it must be one of the protons on the carbon atom next to phosphorus. Its geminal partner is proton C, δ_C = 2.176, J_{CF} = -14.59 Hz and the vicinal coupling constants are 7.48 Hz to D and 2.45 Hz to E. The positions of peaks D and E and the remaining coupling constants were determined iteratively to yield the complete analysis of the spectrum given in Table I.

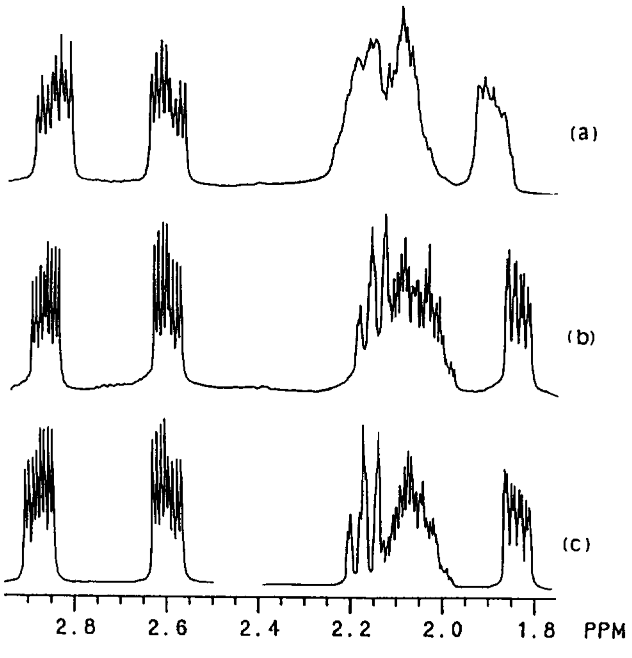


Figure 2. The 500 MHz PMR spectrum of 5-phenyl-1-thia-5-phosphacyclooctane in the aliphatic region. Curve (a) is the experimental spectrum. Curve (b) is the experimental phosphorus-decoupled spectrum, and curve (c) is a theoretical simulation of curve (b).

In an effort to explain the results in Table I, model vicinal coupling constant calculations were made using the program PCMODEL[11], which implements the empirical extension of the Karplus equation proposed by Haasnoot *et al.*[15]. This expression takes into account both the electronegativities of atoms bonded to the carbons bearing the protons of interest and their spatial dispositions. Such calculations clearly show that the molecule cannot have a single, well-defined structure on the NMR time scale because there is no rigid configuration of an SCCCX fragment that will cause geminal methylene protons on a carbon bonded to sulfur to have vicinal methylene coupling constants of 8,3 & 3,8. The experimental constants must therefore be appropriately weighted averages over the eleven conformations shown in Fig. 1.

Accordingly, full sets of vicinal coupling constants and their weighted means were calculated for the six distinguishable protons in each of the six conformers of the molecule having relative energies less than 2 kcal/mol. The weighting factors included both statistical and Boltzmann components. The results, which are presented in Tables II and III, can best be understood by reference to Fig. 3; a perspective view of Conformer I of Fig. 1. The weighted mean coupling constants in Table II permit the unambiguous identifications of protons C, D, E and F as shown in Fig. 3. The identification of protons D and E then allows the unambiguous differentiation of protons A and B on the basis of the weighted mean coupling constants given in Table III.

Table I. The phosphorus decoupled proton magnetic resonance spectrum of I at 500 mHz.

Peak label:		A	B	C	D	E	F
δ/ppm		2.834	2.590	2.176	2.108	2.056	1.883
J_{IJ}/Hz	A		-14.94	0.00	8.28	3.15	0.00
	(or		-14.94		3.15	8.28	)
	B			0.00	3.51	8.35	0.00
	(or				8.35	3.51	)
	C				3.01	11.65	-14.59
	D					-13.76	7.48
	E						2.45

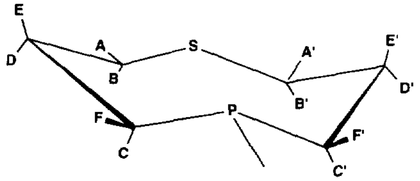


Figure 3. A perspective view of Conformer I

The weighted mean coupling constants given in Tables II and III agree quite well with the experimental ones given in Table I. NMR experiments have shown that in the liquid phase the predominant conformation of the parent hydrocarbon, cyclooctane, is boat-chair, with a few percent of a crown form[16,17]. The behavior of 5-phenyl-1-thia-5-phosphacyclooctane is clearly more complicated.

The PMR Spectrum of trans-1,5-diphenyl-1.5-diphosphacyclooctane 1,5-dioxide

Two isomeric forms of the substance 1,5-diphenyl-1,5-diphosphacyclooctane 1,5-dioxide have been isolated and to some extent characterized both spectroscopically and crystallographically. Both isomers crystallize in the analog of Conformation IV of Fig. 1, which has no molecular symmetry elements. The difference between them is best discussed in terms of an analog of Conformation VI which has the S atom replaced by a P(=O, phenyl) moiety and the lone pair of electrons on the P atom in the 5 position replaced with a doubly-bonded oxygen atom.

MMX calculations show that Conf. VI of the gaseous *trans* isomer would have C_{2h} symmetry. The planes of the two phenyl rings lie in the mirror plane in essentially equatorial positions and the O atoms lie in the mirror plane in essentially axial positions. Conformation VI of a gas phase *cis* isomer would have C_s symmetry.

One phenyl ring is equatorial and its plane lies in the mirror plane. The other phenyl ring is axial with its plane orthogonal to the mirror plane. The existence of two stable isomers immediately rules out any possibility of axial-equatorial interconversion at the phosphorus centers.

The phosphorus-decoupled PMR spectrum of the *trans* isomer in the aliphatic region consists of three four-proton multiplets with chemical shifts of 2.63 (five fully resolved lines), 2.39 (broad with at least five components) and 2.23 (doublet of triplets) ppm. That of the *cis* isomer shows four broad, rather structureless resonances centered on 2.63 (four protons), 2.56 (two protons), 2.19 (four protons) and 2.08 (two protons) ppm.

Because the *trans* isomer has two identical "ends" in Conformation VI, there will be only six different ring conformations with "corners" (disregarding enantiomers). The most stable crown conformation of this isomer has an MMX energy which is 3.4 kcal/mol higher than that of Conformation IV, the global energy minimum. The relative MMX energies of the other discrete conformations are:

Conformation:	IV	V	X	III	II	VI
Rel. Energy in kcal/mol:	0.00	1.54	2.02	3.73	4.04	4.30

Leaving crown conformations aside, the highest energy transition state occurs between Conformations III and IV with a relative energy of 5.5 kcal/mol.

Because of the symmetry of Conformation VI of the *trans* isomer, the four protons on carbons 3 and 7 are both structurally and magnetically equivalent. Enantiomers are readily accessible as the molecule moves on the rather flat potential energy surface, and hence the equivalence of these protons is maintained dynamically even though the lowest energy conformations have no symmetry elements. With this realization it is clear that in agreement with experiment, the phosphorus-decoupled PMR spectrum of this isomer will exhibit three unique proton chemical shifts with equal integrated areas.

According to this model the protons labeled C, A, C' and A' in the pertinent analog of Fig. 3 would all have the same chemical shift as one another. Their geminal partners, B, F, B' and F' would have a different one, as would the protons D, E, D' and E' that are vicinal to both of the other two sets of four equivalent protons.

If only Conformation IV of this fluxional molecule was significantly populated, the two mean vicinal coupling constants could be calculated by creating a one-rowed analog to Tables II and III containing sixteen vicinal coupling constants for Conformation IV of Compound II similar in magnitude but not identical to those given for this conformation of Compound I in Tables II and III. One of the two "experimental" vicinal coupling constants would then be calculated by adding together the entries in this one-rowed table for protons A, C, A', C' and dividing the resulting sum by eight. The other would be calculated by taking one-eighth of the sum of the remaining eight entries.

Such a calculation yields theoretical vicinal coupling constants of 8.09 Hz for the set of four protons of type A,C, and 4.01 Hz for those of type B,F. The Boltzmann factors for Conformations V and X are such that they should also be included in the averaging process. Conformations IV and V can be achieved in twice as many ways as can Conformation X so both statistical and Boltzmann weighting are required (cf. the footnotes to Tables II and III.). The resulting doubly-weighted mean vicinal coupling constants are 7.95 Hz for the type A,C protons and 4.16 Hz for those of type B,F. If the three lowest-lying conformations had equal energies but unequal statistical weights, the resulting coupling constants would be 6.93 Hz and 5.35 Hz, respectively.

Spectral simulation gave experimental vicinal coupling constants of 6.97 Hz for the protons at 2.65 ppm to those at 2.39 ppm and 4.87 Hz for the protons at 2.23 ppm to those at 2.39 ppm. The geminal coupling constant for the protons on the four ring carbon atoms adjacent to phosphorus is -14.9 ppm. It is interesting to note that the experimental values lie between those calculated with and without Boltzmann factor weightings. This behavior may imply that the relative energies of the conformers in solution differ slightly from those calculated by MMX methods. It is virtually certain, however that the predominant conformation of the molecule

Table II. Coupling Constant Calculation For The Protons Proximal To Phosphorus In 5-Phenyl-1-Thia-5-Phosphacyclooctane.

CONF.[a]	WF[b]	RE[c]	BF[d]	(C,E)	(C',E')	(C,D)	(C',D')	(F,E)	(F'E')	(F,D)	(F',D')
I	1	0	1.000	13.95	13.66	3.25	0.80	3.11	0.73	3.91	7.39
II	2	0	1.000	14.07	4.25	2.54	3.22	2.54	3.06	4.66	13.89
V	2	510	0.425	13.22	11.14	5.19	0.25	4.85	0.17	2.22	11.14
IV	2	910	0.217	12.87	14.08	5.67	1.62	5.47	1.67	1.88	6.15
VII	2	1360	0.102	12.79	1.95	5.88	5.84	5.70	5.69	1.65	12.53
VIII	2	1810	0.048	13.94	10.97	3.41	0.15	3.02	0.11	3.88	11.80
WTD MEAN COUPLING CONST[e]				11.13		2.80		2.73		7.38	

[a] Conformation number according to Figure 2.
[b] Statistical weighting factor; i.e., the (relative) number of structures with the conformation in question.
[c] Energies of the conformations in question with conformation I as the defined energy zero; given in cal/mol.
[d] Boltzmann factors at 300 K. BF=EXP{-RE/(1.987*300)}.
[e] Calculated as Σ{[WF*BF*J(P,Q)]+[WF*BF*J(P',Q')]}/{2*ΣWF*BF}

Table III. Coupling Constant Calculation For The Protons Proximal To Sulfur In 5-Phenyl-1-Thia-5-Phosphacyclooctane.

CONF.[a]	WF[b]	RE[c]	BF[d]	(B,E)	(B',E')	(B,D)	(B',D')	(A,E)	(A'E')	(A,D)	(A',D')
I	1	0	1.000	12.38	12.94	0.86	3.05	0.84	3.14	6.89	3.63
II	2	0	1.000	13.02	3.83	2.48	3.23	2.45	2.83	4.43	12.93
V	2	510	0.425	2.21	11.37	4.59	5.72	4.64	6.37–	12.42	1.43
IV	2	910	0.217	4.72	9.16	2.18	0.80	2.35	0.88	13.02	10.76
VII	2	1360	0.102	2.89	10.22	3.82	0.54	3.88	0.62	12.72	9.79
VIII	2	1810	0.048	2.91	6.46	3.72	1.33	3.77	1.06	12.79	12.79
WTD MEAN COUPLING CONST[e]				8.74		2.92		2.91		8.1	

[a] Conformation number according to Figure 2.
[b] Statistical weighting factor; i.e., the (relative) number of structures with the conformation in question.
[c] Energies of the conformations in question with conformation I as the defined energy zero; given in cal/mol.
[d] Boltzmann factors at 300 K. BF=EXP{-RE/(1.987*300)}.
[e] Calculated as Σ{[WF*BF*J(P,Q)]+[WF*BF*J(P',Q')]}/{2*ΣWF*BF}

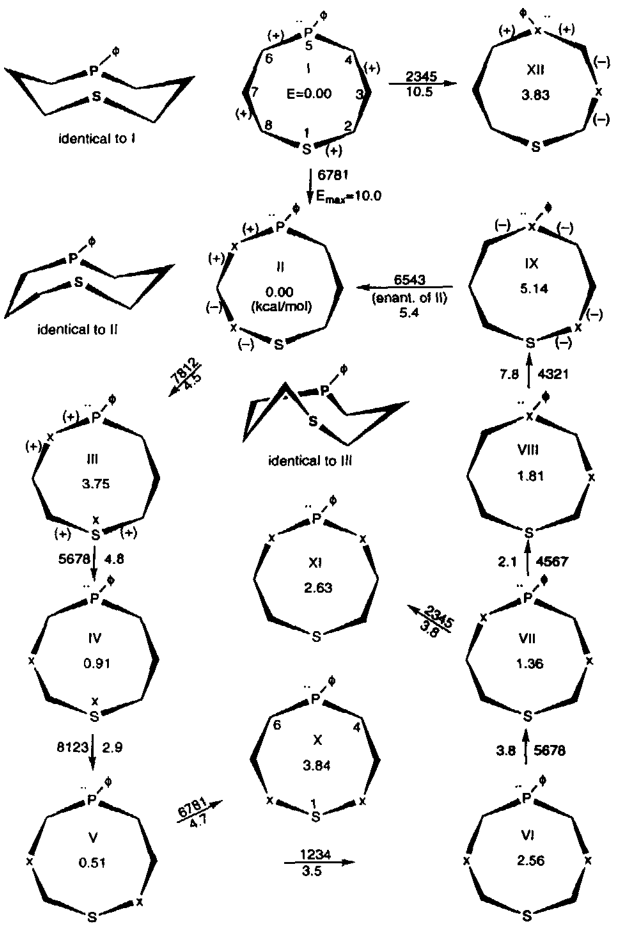


Fig. 1. Conformational potential energy surface of 5-phenyl-1-thia-5-phosphacyclooctane.

in solution is the same unsymmetrical boat-chair in which it crystallizes, along with a small amount of a twist boat chair. The crown form is probably absent because the mean BF coupling constant for such a conformation would be about 1 Hz smaller than the experimentally observed value.

The PMR Spectrum of 1,5-dithiacyclooctane (1,5-DTCO)

The PMR spectrum of 1,5-DTCO dissolved in chloroform and measured at 300 MHz consists simply of two multiplets: $\delta = 2.06$ ppm, 7 resolved lines, relative area = 1; and $\delta = 2.82$, 5 resolved lines, relative area = 2. Such a simple spectrum clearly implies the presence of only two different kinds of protons: the eight next to sulfur in one class and the four on carbons 3 and 7 in the other. In other words, in contrast to the other two compounds discussed above, 1,5-DTCO is fully fluxional. It undergoes both pseudorotation and ring inversion.

The experimental spectrum could be reproduced essentially perfectly with a spectral simulation of one "half" of the molecule in which each proton in two geminal pairs of four magnetically equivalent protons was coupled to each of two equivalent vicinal protons. The resulting coupling constants were 8.156 and 3.560 Hz.

MMX calculations yielded essentially the same energies for Conformations I and II, with those of Conformations V(=VII) and IV(=VIII) being higher by 590 and 1100 cal/mol, respectively. The existence of only two kinds of protons implies that the time-averaged behavior of the eight protons on methylenes next to phosphorus can be modeled simply by considering the coupling of protons C and F to D and E in a figure similar to Fig. 3.

The calculated weighted mean of the six values of J_{CE} for 1,5-DTCO is $<J_{CE}>=12.82$ Hz (cf. column 5 in Table II). The analogous $<J_{FE}>=3.48$ Hz, so proton "E" experiences an overall average coupling constant of (12.82+3.48)/2=8.15 Hz to that geminal pair. For proton "D" an analogous calculation gives an overall average coupling constant of (3.40+3.45)/2=3.43 Hz to the C,F geminal pair. The agreement between the observed and calculated coupling constants is quite satisfactory.

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