Sephadex. The amino acid composition of the purified fragments was in good agreement with that of amino acid sequences as proposed in Figure 1. Thus, the disulfide bridges are formed by residues 68–162 and 179–186. The single tryptophan residue is in position 25. The three histidine residues are in positions 33, 36, and 148. Studies on structure–activity relationship of the HGH molecule are in progress.[16]

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The Structure of $(NPCl_2)_5$. A Ten-Membered Phosphorus–Nitrogen Ring[1]

Sir:

The crystal structures of two members of the $(NPCl_2)_n$ series, namely the trimer[2] and tetramer,[3] have been previously determined. While these structure determinations have been useful in partially elucidating the bonding in the phosphonitrilic chloride series, there still remain points of controversy[4–6] which we felt might be clarified by a structure determination of a higher member of this series. In particular, in the larger rings there are many more configurations which the molecule might assume, making the chosen configuration all the more interesting.

We have now essentially completed the single-crystal, X-ray study of $(NPCl_2)_5$. The crystals are orthorhombic with four molecules in a unit cell of dimensions: $a = 15.48$, $b = 19.44$, and $c = 6.26$ A, and with space group symmetry $P2_12_12_1$. Three-dimensional data were collected using Mo Kα radiation with a General Electric XRD-5 X-ray unit equipped with a single-crystal orienter. The 1319 observed reflections were used to generate a sharpened Patterson. The Patterson function was deconvoluted using a symmetry map (first-order consistency function) generated from the three Harker sections[7] and employing superposition methods along with successive electron density map calculations. Isotropic refinement lowered the reliability factor, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, to 0.15 based on all observed data. Further anisotropic refinement resulted in a decrease in this factor to a final value of 0.08. Details of the structure determination and refinement will be reported later.

Decachloropentaphosphonitrile exists as a ten-membered ring consisting of alternating phosphorus and nitrogen atoms, with two chlorine atoms attached to each phosphorus (see Figure 1). The ten atoms forming the ring lie surprisingly close to their least-squares plane. Only one atom, P(5), is off the plane by more than 0.2 A, and only four (P(5), P(3), N(4), and N(5)) are off by more than 0.1 A. The five nitrogen atoms define very well a plane, the greatest deviation from this least-squares plane being less than 0.05-A. The Cl–P–Cl and N–P–N angles are consistent with those observed in the trimer and tetramer, being 102.0° and 118.4°, respectively. The P–Cl distances found in the pentamer were slightly shorter than those in the other compounds, ranging from 1.94 to 1.98 A. However, when thermal corrections are applied, the actual deviations will be smaller and the average distance will be closer to the 1.985 observed in the trimer and tetramer. A more serious disparity between the pentamer and the others is seen in the P–N distances and the P–N–P angles. The distances range from 1.49 to 1.55 A, but in no systematic way as to imply alternating double-bond character. The average P–N distance of 1.52 A is considerably shorter than the 1.59 observed in the trimer and 1.58 found in the tetramer. The average P–N–P angle in the pentamer is 148°, 16° greater than in the tetramer. Because this angle has opened up to such an extent, the pentamer is able to remain nearly planar. These observations seem to imply that the π character of the molecule requires a planar configuration and further that the π-bond character increases with increasing ring size. A more complete discussion of the structure and of the bonding as related to the structures of the lower members of the series will be reported later.

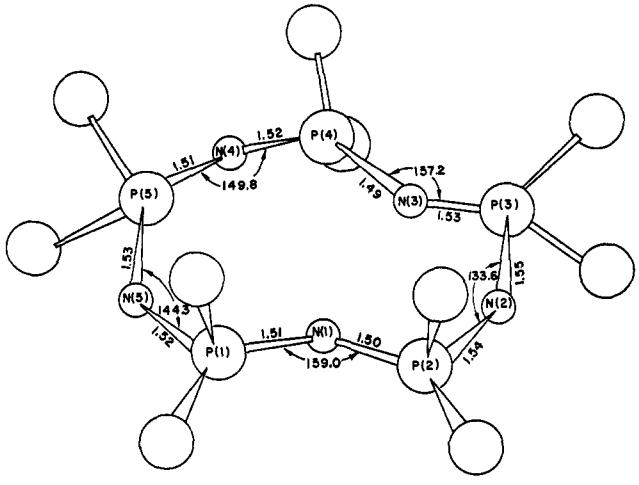

Figure 1. The molecular configuration of $(NPCl_2)_5$.

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Steric Inhibition of the Interaction of a Cyclopropyl Substituent with the Electron-Deficient Center in the Solvolysis of *t*-Cumyl Derivatives

Sir:

There is increasing evidence that the maximum interaction between a cyclopropane group and an adjacent

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Table I. Rate Constants and Derived Data for the Solvolysis of *t*-Cumyl Chlorides in 90% Aqueous Dioxane at 25°

t-Cumyl chloride	Rate constant, $k_1 \times 10^5$ sec^{-1}	Rel. rate	Effect of substituent	ΔH^*	ΔS^*
Hydrogen	12.4	1.00		18.8	−12.4
4-Isopropyl	221	17.8	17.8	17.4	−12.4
3-Methyl[a]	24.8	2.00	2.0	18.6	−11.8
4-Cyclopropyl	1947	157[b]	157	16.1	−12.4
3-Methyl-4-cyclopropyl	2133	172[b]	86	16.0	−12.5
3,5-Dimethyl[c]	47.3	3.9			
3,5-Dimethyl-4-cyclopropyl	460	37.1[b]	9	16.9	−12.6

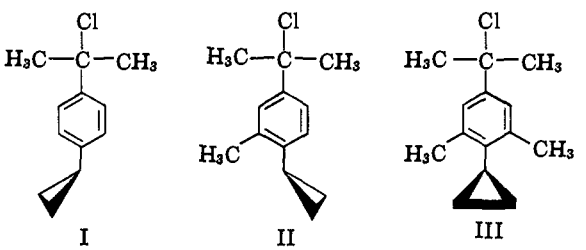
[a] Reference 7. [b] Extrapolated from data at lower temperatures. [c] Reference 8.

electron-deficient center is achieved with the bisected conformation predicted by the Walsh model.[1-5] We wish to report that the large electronic contributions of the cyclopropyl substituent in *p*-cyclopropyl-*t*-cumyl chloride[6] are lost in the presence of methyl substituents, *ortho* to the cyclopropyl group, which prevent the cyclopropyl substituent from achieving this bisected arrangement. Indeed, under these circumstances the effect of the *p*-cyclopropyl substituent becomes even smaller than that of a representative alkyl group, such as *p*-isopropyl.

A *p*-isopropyl substituent increases the rate of solvolysis of *t*-cumyl chloride in 90% aqueous acetone at 25° by a factor of 18.[7] On the other hand, a *p*-cyclopropyl substituent is much more effective—it increases the rate by a factor of 157. A single *o*-methyl substituent, as in 3-methyl-4-cyclopropyl-*t*-cumyl chloride, increases the relative rate to 172. Correcting for the contribution of the *m*-methyl substituent, a factor of 2,[7] reveals only a modest decrease in the effect of the cyclopropyl group accompanying the introduction of the single methyl substituent. On the other hand, the observed relative rate for 3,5-dimethyl-4-cyclopropyl-*t*-cumyl chloride is 37. Correcting this value for the contribution of the two *o*-methyl substituents, a factor of 4,[8] reveals a relatively sharp drop in the contribution of the cyclopropyl substituent to the rate, to a factor of only 9. Thus, with two *o*-methyl substituents, the contribution of the *p*-cyclopropyl substituent to the rate drops from its original high value of 157 down to a low value of 9, even lower than the effect of a simple alkyl substituent, such as 18 for *p*-isopropyl.

The experimental data are summarized in Table I.

An examination of structures I–III reveals that the bisected structure (I) in the transition state would not be seriously affected by a single *o*-methyl substituent, since the cyclopropyl group would be free to rotate 180° to achieve the bisected conformation on the other side of the aromatic ring (II). However, two *o*-methyl substituents would effectively block this conformation (III). Consequently, the data support the bisected conformation in the transition states and further reveal that failure to achieve this conformation reduces the



I II III

electronic contribution from the cyclopropyl substituent to a value well below that realized from simple alkyl substituents in the same system.

Cyclopropylbenzene, *o*-methylcyclopropylbenzene, and 2,6-dimethylcyclopropylbenzene were prepared by the reaction of the corresponding styrenes with the Simmons–Smith reagent. Aluminum chloride catalyzed acetylation of the hydrocarbons in chloroform at −40° yielded respectively: *p*-cyclopropylacetophenone;[6] 3-methyl-4-cyclopropylacetophenone, bp 112° (1 mm), n^{20}D 1.5610, dinitrophenylhydrazone mp 215°; and a mixture, 15% 3,5-dimethyl-4-cyclopropylacetophenone, n^{20}D 1.5511, 2,4-DNP mp 234–235°, and 85% 2,4-dimethyl-3-cyclopropylacetophenone, n^{22}D 1.5493, 2,4-DNP mp 210–211°. This is to be contrasted with the formation of 79% of the symmetrical isomer in the acetylation of 1,2,3-trimethylbenzene,[9] confirming the great reduction in the directive influence of the cyclopropyl substituent when flanked by two methyl groups. Treatment of the acetophenones with methylmagnesium iodide yielded: *p*-cyclopropyl-α-methylstyrene, bp 84–85° (1 mm), n^{20}D 1.5625; 3-methyl-4-cyclopropyl-α-methylstyrene, n^{22}D 1.5554; 3,5-dimethyl-4-cyclopropyl-α-methylstyrene, n^{22}D 1.5518.[10] The olefins were converted into the chlorides by treatment with hydrogen chloride in methylene chloride, using the new automatic hydrochlorination procedure.[11] Nmr examination established that in each of the three cases both the conversion to the chloride and the solvolysis to a mixture of olefin and alcohol proceeded without opening of the cyclopropane ring.

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