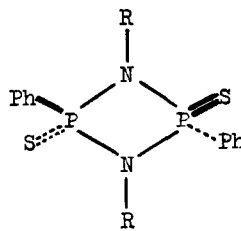
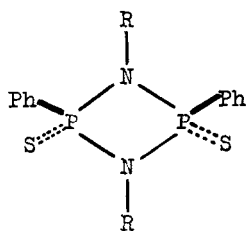


cis- AND trans- 1,3-DIETHYL-2,4-DIPHENYL-2,4-DITHIOCYCLODIPHOSPHAZANES

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PHENYLPHOSPHONOTHIOIC DIAMIDES, $\text{PhP}(:\text{S})(\text{NHR})_2$ (I), undergo condensation reactions on thermolysis. The diamino-derivative (I, R = H), forms a cyclic triphosphazane,¹ whereas alkylamides (I, R = Alk) tend to form cyclic diphosphazanes.^{1,2} It is clear that cyclodiphosphazanes might occur as geometrical isomers with like groups attached to phosphorus in cis- (II) or trans- (III) positions. Trippett prepared methyl- and benzyl-derivatives and suggested that their ¹H n.m.r. spectra during purification indicated mixtures of isomers.²



We report here the preparation of two ethyl-

derivatives, whose compositions were confirmed by analysis and mass spectrometry, which are the first example of geometrical isomers of this type. The parent compound (I, R = Et) was heated at 180-200°/5 hr. The glassy residue dissolved in benzene, and chromatography on a silica column gave the 1,3-diethyl-2,4-diphenyl-2,4-dithiocyclodiphosphazanes.³ The isomers have different ¹H n.m.r. and ultraviolet spectra, and they can be distinguished by comparisons of their infrared and Raman spectra. The cis-derivatives can have only mirror symmetry, whereas the trans-derivatives are approximately centrosymmetric if the four-membered ring is planar. Even if there is an appreciable departure from planarity, this probably will have little effect on the vibrational spectra. The infrared and Raman spectra of the compound to which a cis-structure is assigned (II, R = Et), m.p. 134°, have nine bands at the same energy ($\pm 3 \text{ cm}^{-1}$) in the range 100-1200 cm^{-1} . The spectra of the trans-compound (III, R = Et), m.p. 142°, show no coincidences.

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¹ E. H. M. Ibrahim and R. A. Shaw, Chem. Comm., 244 (1967)

² S. Trippett, J. Chem. Soc., 4731 (1962)

³ For nomenclature see R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, Chem. Rev., 62, 247 (1962)