Studies in Cyclophosphazenes. Part 8.[1] The Equilibria between Isomeric Non-geminal Aminochlorocyclotriphosphazenes

By **Nizza Friedman, Jacob M. E. Goldschmidt,* Uri Sadeh,** and **Miriam Segev,** Department of Chemistry, Bar-Ilan University, Ramat-Gan, 52100 Israel

The *cis* and *trans* isomers of three pairs of non-geminal chloro(dimethylamino)cyclotriphosphazenes $N_3P_3Cl_{6-n}(NMe_2)_n$ with n = 2, 3, or 4 have been allowed to equilibrate in two solvents at several temperatures using dimethylamine hydrochloride as catalyst, and then the isomer ratios were determined using gas chromatographic analysis. Values of ΔH and ΔS for the equilibria have been evaluated. As solvent effects appear to exceed inter-substituent interactions, no conclusions on the planarity of the cyclotriphosphazene ring can be drawn from the results. Consideration of the relative rates of the isomerization reactions of compounds with different degrees of substitution reveals differences in their mechanisms and supports the operation of certain mechanisms proposed earlier.

THE isomerization reactions of non-geminally substituted cyclotriphosphazenes in general [2] and specifically of non-geminal aminochlorocyclotriphosphazenes [3,4] have been reviewed. Catalysis of the latter reactions by amine hydrochloride,[5] aluminium chloride,[6] hydrogen chloride,[7] and by bases (for alkylamino-derivatives only) [8] is known to occur with specific compounds, but the absence of isomerization was noted with other compounds.[5,6] The reported failure to detect isomerization is, in particular cases, now known to stem from shortcomings of the analytical methods applied and isomerization actually does occur.[1] Only two studies of isomer ratios at equilibrium seem to have been reported.[9,10]

This report is a continuation of our previous preliminary study [10] of the equilibrium involving one pair of isomers. We have now extended our research to cover measurements of the equilibria attained at several temperatures, in two solvents, between the *cis* and *trans* isomers of the following: 2,2,4,6-tetrachloro-4,6-bis(dimethylamino)cyclotriphosphazene, (I); 2,4,6-trichloro-2,4,6-tris(dimethylamino)cyclotriphosphazene, (II); and 2,4-dichloro-2,4,6,6-tetrakis(dimethylamino)-cyclotriphosphazene, (III). All these compounds are known to undergo isomerization.[1,5,6,10] Our aim was to clarify the question of the planarity of the cyclotriphosphazene ring $(PN)_3$.

Interest in this question, stimulated by comparisons of the electron delocalization in cyclotriphosphazenes with the aromaticity of benzene and its derivatives, has prompted much research. Most structural determinations of cyclotriphosphazenes in the literature,[2,11a] performed on solid compounds by *X*-ray diffraction, show that generally $(PN)_3$ rings are only approximately planar. The relatively slight non-planarity is real though, clearly being greater than the experimental uncertainties, and it has often been ascribed to crystal-packing effects.

Data on the shape of the $(PN)_3$ ring in the gaseous, liquid, or dissolved states in which intermolecular interactions are, of course, reduced or totally absent, is sparse. In the only electron-diffraction study,[12] of three reported,[12-14] in which non-planarity was considered, significant deviation of the ring from planarity was observed. Other evidence for possible non-planarity in $(PN)_3$ rings is indirect and debatable: (1) in all of several dipole-moment measurements of $(NPCl_2)_3$ in solution [15-17] and in melts,[17] non-zero values were obtained; (2) unexpected features in the ^1H n.m.r. spectra of 2,2-diamino-4,4,6,6-tetrakis(dimethylamino)cyclotriphosphazene [18,19] and of pentachloro(dimethylamino)cyclotriphosphazene [20] have been ascribed to non-planarity of the ring; (3) finally data for the equilibrium between *cis*- and *trans*-2,2,4,6-tetrachloro-4,6-bis(dimethylamino)cyclotriphosphazenes have been rationalized by assuming a chair-like conformation of the $(PN)_3$ ring.[10] In order to try and answer this question, we have now studied the effect of varying the degree of substitution in aminochlorocyclotriphosphazenes on the isomeric equilibria between them in solution.

EXPERIMENTAL

Materials.—Published procedures were used to synthesize *cis*-[21] and *trans*-[22] 2,4,6,6-tetrachloro-2,4-bis(dimethylamino)-, *trans*-[22] 2,4,6-trichloro-2,4,6-tris(dimethylamino)-, and *cis*-[22] and *trans*-[1] 2,4-dichloro-2,4,6,6-tetrakis(dimethylamino)-cyclotriphosphazenes. The preparation of *cis*-2,4,6-trichloro-2,4,6-tris(dimethylamino)cyclotriphosphazene was carried out in acetonitrile to produce roughly equal amounts of the crude *cis* and *trans* isomers.[23] These were separated by a known method.[22] The dimethylamine hydrochloride (Merck) used as catalyst was carefully dried and stored over phosphorus pentaoxide. Acetonitrile (Merck) was refluxed over P_2O_5 and distilled, the fraction boiling between 81 and 82 °C being collected. The alcohol in chloroform (Frutarom) was removed by repeated extraction with water. The solvent, after drying over anhydrous calcium chloride, was distilled, the fraction boiling in the range 59—61 °C being used.

Instrumentation.—For experiments with compound (I) an F & M model 720 gas chromatograph was employed. Glass columns (length, 4 m) were filled with acid-washed Chromasorb W (60—80 mesh) (Johns Manville) that was loaded with 2.7% SE-52 silicone oil. The column temperature was 155 °C. The carrier gas used was helium at a flow rate of 85 $cm^3\ min^{-1}$. A thermal-conductivity detector operating between 250 and 280 °C was used. Peak areas were measured by an Infotronics CRS-100 integrator. With this detector, calibration of peak areas was found unnecessary. For determinations of the isomer ratios of compounds (II)

and (III) a Packard 873 gas chromatograph fitted with a flame-ionization detector was used. This was coupled to an Autolab System IV integrator (Spectra-Physics Inc.). For the gas chromatographic (g.c.) analysis of (II), 2-m glass columns filled with acid-washed Chromasorb W (60—80 mesh) loaded with 8% SE-30 were employed. The oven temperature was 180 °C and the nitrogen carrier-gas flow rate was 30 cm^3 min^{-1}. For (III) the glass columns were 1 m long and were filled with the same solid support but loaded with 8% HI-EFF (Applied Science Laboratories). The oven temperature was 150 °C and the nitrogen carrier-gas flow rate was 40 cm^3 min^{-1}. Peak areas were calibrated daily immediately before determinations were made.

Isomerizations.—Taking stringent precautions to assure the exclusion of moisture, acetonitrile or chloroform (*ca.* 5 cm^3) was added by syringe to vessels that contained weighed samples (*ca.* 50—100 mg) of the aminochlorocyclotriphosphazenes and dried dimethylamine hydrochloride (*ca.* 50 mg). (In certain repeat runs, instead of using isomerically pure starting materials, mixtures that initially contained an excess of one or the other of the starting isomeric phosphazenes were used.) The closed glass vessels were fitted with Teflon stopcocks and septa enabling the introduction of solvent and the removal of samples without there being any need to expose their contents to moist air. The solutions in the vessels were immersed in thermostat baths (±0.5 °C) held at the various temperatures. In the extended experiments some loss of solvent was noted. These losses were periodically made up with fresh solvent injected through the septa. From time to time samples were removed with the aid of microsyringes fitted with extra-long needles and injected directly into the gas chromatograph. In the case of compound (III) this simple procedure could not be used as the amine hydrochloride present was found to cause isomerization on the g.c. columns. [This effect was proved absent for (I) and (II).] To overcome this complication the samples removed were treated as follows. First the solvent was evaporated off rapidly, then the phosphazene was extracted with diethyl ether, and finally the ether solutions were subjected to g.c. analysis. Equilibrium was considered achieved when the averages of the ratios, as determined by a number of injections of solutions that initially contained the *cis* or the *trans* isomers, reached the same value within experimental error.

RESULTS AND DISCUSSION

Table 1 presents data on the equilibria attained at several temperatures in two solvents between the *cis* and *trans* isomers of (I), (II), and (III) in solutions that originally contained *cis* and *trans* isomers. The values of ΔH and ΔS calculated from the equilibrium data of Table 1 appear in Table 2. All values of K, the equilibrium constant, are close to unity showing that there are only small differences in the stabilities of the isomers under the conditions prevailing in the experiments. Inevitably these values of K lead to relatively large limits of uncertainty in K. Similarly, the relative errors associated with ΔH and ΔS are also large, a fact aggravated by their small values.

TABLE 1

Data [a] on equilibria attained between non-geminal chloro(dimethylamino)cyclotriphosphazenes at various temperatures in acetonitrile and chloroform

		$N_3P_3Cl_4(NMe_2)_2$				$N_3P_3Cl_3(NMe_2)_3$				$N_3P_3Cl_2(NMe_2)_4$			
		% *trans* isomer starting from				% *trans* isomer starting from				% *trans* isomer starting from			
Solvent	*T*/K	*trans*	*cis*	K [b]	ΔG/ J mol^{-1}	*trans*	*cis*	K [b]	ΔG/ J mol^{-1}	*trans*	*cis*	K [b]	ΔG/ J mol^{-1}
Acetonitrile	308									58.5 ±1.0	58.4 ±0.8	1.41 ±0.05	−870 ±100
	313.5	53.5 ±0.8	53.5 ±0.8	1.15 ±0.04	−360 ±80								
	331.5	54.7 ±0.6	54.8 ±0.8	1.21 ±0.03	−520 ±80								
	338									60.0 ±0.2	60.0 ±0.7	1.50 ±0.03	−1 140 ±70
	349.5	55.9 ±0.8	55.7 ±0.7	1.26 ±0.04	−670 ±90								
Chloroform	303					60.5 ±0.7	60.0 ±0.4	1.53 ±0.04	−1 070 ±65				
	308									56.8 ±0.7	57.0 ±0.3	1.32 ±0.03	−710 ±60
	323									64.9 ±0.5	65.0 ±0.7	1.88 ±0.06	−1 700 ±80
	331					69.6 ±0.2	69.8 ±0.3	2.30 ±0.03	−2 290 ±33				
	331.5	56.2 ±1.1	56.2 ±1.0	1.28 ±0.05	−680 ±120								

[a] Limits of uncertainty are standard deviations. [b] For reaction *cis* isomer ⇌ *trans* isomer.

Information on the shape of the $(PN)_3$ ring should be provided by comparison of the values of ΔH observed with those predicted by considering inter-substituent contacts in planar and chair-like puckered structures. Considering all non-geminal isomers with chloro- and dimethylamino-substituents, *i.e.* $N_3P_3Cl_{6-n}(NMe_2)_n$ with $n = 2$, 3, or 4, for planar structures the enthalpies of the *trans* isomers, H_{trans}, should be lower than those of the *cis* isomers, H_{cis}, because more of the bulkier dimethyl-

amino-groups are on the same side of the ring in the *cis* than in the *trans* isomers. This will lead to negative values of ΔH defining K as [*trans*]/[*cis*]. In contrast, in chair-like puckered structures H_{trans} should exceed H_{cis} and ΔH will be positive as more of the larger groups are axial in the *trans* than in the *cis* isomers. Inspection of the values of ΔH in Table 2 *a priori* supports the non-planar ring structure, but comparison of ΔH values for compound (III) in the two solvents indicates significant solvent effects. As *cis* isomers are more polar than *trans* isomers,[24] solvation will stabilize them to a greater extent and the values of ΔH found can equally well be ascribed to solvation. Moreover, the values of ΔS are fully consistent with the latter interpretation. The proposals made in our previous study are, therefore, not substantiated and attempts to draw conclusions on the planarity of the $(PN)_3$ ring from equilibrium data as measured in solution appear unjustified.

TABLE 2

Values * of ΔH and ΔS for equilibria between non-geminal *cis*- and *trans*-chloro(dimethylamino)cyclotriphosphazenes in acetonitrile and chloroform

	$N_3P_3Cl_4(NMe_2)_2$		$N_3P_3Cl_3(NMe_2)_3$		$N_3P_3Cl_2(NMe_2)_4$	
Solvent	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	ΔH/kJ mol^{-1}	ΔS/J K^{-1} mol^{-1}
Acetonitrile	2.3 ± 1.7	8.4 ± 4.6			2.1 ± 1.0	9.2 ± 3.3
Chloroform			12.2 ± 0.8	43.5 ± 2.5	19.7 ± 2.1	64.9 ± 6.3

* Limits of uncertainty are standard deviations.

The small differences in the stabilities of the isomers imply the absence of appreciable transannular contacts as found in *X*-ray structural determinations,[25] and consequently they support the suggestions made that the ring non-planarity in the crystalline state arises primarily from intermolecular interactions. The observed operation of appreciable solvent effects conforms with known observations on the replacement reactions of the cyclotriphosphazenes.[4,23,26]

Two extreme mechanisms, for the isomerization reactions of aminochlorocyclotriphosphazenes, nucleophilic attack by chloride ions and ionization of chloride ions, and combinations of these, have been discussed.[5,6,11b] The relative rates of isomerization estimated from the times needed to reach equilibrium beginning from the *pure* isomers, as recorded in the present study, are relevant to these mechanistic proposals. The isomerization of compound (I) took 1—2 months to reach equilibrium; (II) required 4—5 months to do so, whilst surprisingly with (III) equilibrium was attained in 1—2 d. Since the concentrations of the reagents and the temperatures were all in the same ranges, the relative rates of isomerization under the above conditions are clearly (III) > (I) > (II).

Comparing (I) with (II), the additional dimethylamino-group in the latter causes increased mesomeric charge transfer to the $(PN)_3$ ring and reduces its electrophilicity.[26,27] Then the relative rates of isomerization of the two isomers can be rationalized by invoking the mechanism in which nucleophilic attack by chloride ion is the rate-determining step. This was first proposed by Sowerby [28] for chlorine exchange in hexachlorocyclotriphosphazene: the relatively more rapid rate of this last reaction involving the 'unsubstituted' ring, with measured half-times being in the range 8—116 min, is consistent with the trend predictable for this mechanism.

The faster isomerization of (III) relative to (I) and (II), clearly irreconcilable with the above reasoning, is plausible in terms of a mechanism in which at least partial ionization initiates the reaction irrespective of whether this is a pre-equilibrium or the rate-limiting step. The electron release of the four dimethylamino-groups presumably effectively inhibits attack by chloride ion but promotes ionization and explains the change in mechanism. The results of the following qualitative kinetic experiments performed on (III) support * the ionization mechanism and give an indication of electrophilic assistance by $NMe_2H_2^+$ attacking the chlorine atom exchanged: (1) the rate of isomerization was found to be proportional to the concentration of amine hydrochloride; (2) the presence of water in the acetonitrile was found to catalyze the isomerization very appreciably; (3) hydrogen chloride dissolved in acetonitrile (in the absence of water) inhibited isomerization very appreciably. Since a 'pure' rate-determining ionization mechanism requires kinetics independent of salt concentration, the postulated electrophilic assistance explains the dependence found, notwithstanding any involvement of chloride ion in other stages of the reaction. Increased polarity of the medium, promoting ionization, explains the catalytic effect of water, but higher solubility of the salt, with water present, may contribute. The retardation caused by hydrogen chloride can be ascribed to two effects. The primary one involves protonation of (III) which is known to be appreciably basic.[29] This retards ionization but would accelerate the reaction if chloride-ion attack were involved. The second effect stems from a reduction in the concentration of $NMe_2H_2^+$ because of increased ion-pair formation with the added chloride ions.

* We acknowledge the comment of a referee who pointed out that the ionization mechanism generating charge in the transition state will be expected to be very sensitive to salt concentration as well as solvent polarity, as found. The effect of added $NMe_2H_2^+$ does not therefore have to be a catalytic one.

[9/1513 *Received*, 24*th September*, 1979]

REFERENCES

[1] Part 7, J. M. E. Goldschmidt and U. Sadeh, *J. Inorg. Nuclear Chem.*, 1980, **42**, 618.

[2] S. S. Krishnamurthy, A. C. Sau, and M. Woods, *Adv. Inorg. Radiochem.*, 1978, **21**, 41.
[3] J. M. E. Goldschmidt, in 'Analytical Chemistry of Phosphorus Compounds,' ed. M. Halman, Wiley, New York, 1972, p. 523.
[4] R. A. Shaw, *Z. Naturforsch.*, 1976, **B31**, 641.
[5] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 4067.
[6] R. Keat, R. A. Shaw, and C. Stratton, *J. Chem. Soc.*, 1965, 2223.
[7] S. N. Nabi, R. A. Shaw, and C. Stratton, *J.C.S. Dalton*, 1975, 588.
[8] Z. Gabay and J. M. E. Goldschmidt, unpublished work.
[9] C.M. Sharts, A. J. Bilbo, and D. R. Gentry, *Inorg. Chem.*, 1966, **5**, 2140.
[10] J. M. E. Goldschmidt and M. Segev, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 163.
[11] H. R. Allcock, ' Phosphorus–Nitrogen Compounds,' Academic Press, New York, 1972, (*a*) p. 385; (*b*) p. 272.
[12] M. I. Davis and J. W. Paul, *J. Mol. Structure*, 1972, **12**, 249.
[13] L. O. Brockway and W. M. Bright, *J. Amer. Chem. Soc.*, 1943, **65**, 1551.
[14] M. I. Davis and J. W. Paul, *J. Mol. Structure*, 1971, **9**, 478.
[15] H. J. Krause, *Z. Electrochem.*, 1955, **59**, 1004.
[16] G. Corfield, *J. Chem. Soc.*, 1962, 4258.
[17] H. R. Allcock and R. J. Best, *Canad. J. Chem.*, 1964, **42**, 447.
[18] C. T. Ford, F. E. Dickson, and I. I. Bezman, *Inorg. Chem.*, 1964, **3**, 177.
[19] G. R. Feistel and T. Moeller, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2731.
[20] G. R. Feistel, Ph.D. Thesis, University of Illinois, 1965.
[21] Z. Biran and J. M. E. Goldschmidt, *Synth. React. Inorg. Met.-Org. Chem.*, 1978, **8**, 185.
[22] R. Keat and R. A. Shaw, *J. Chem. Soc.*, 1965, 2215.
[23] J. M. E. Goldschmidt and M. Segev, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 161.
[24] H. Koopman, F. J. Spruit, F. Van Deursen, and J. Bakker, *Rec. Trav. chim.*, 1965, **84**, 341.
[25] F. R. Ahmed and D. R. Pollard, *Acta Cryst.*, 1972, **B28**, 513, 3530; F. R. Ahmed and E. J. Gabe, *ibid.*, 1975, **B31**, 1028; F. R. Ahmed and S. Fortier, *ibid.*, 1980, **B36**, 1456.
[26] J. M. E. Goldschmidt and E. Licht, *J. Chem. Soc.* (*A*), 1971, 2429.
[27] M. Becke-Goehring, K. John, and E. Fluck, *Z. anorg. Chem.*, 1959, **302**, 103; B. Capon, K. Hills, and R. A. Shaw, *J. Chem. Soc.*, 1965, 4059.
[28] D. B. Sowerby, *J. Chem. Soc.*, 1965, 1396.
[29] D. Feakins, W. A. Last, S. N. Nabi, and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 1831.