Structures and Properties of Isomeric Cyclodiphosph(III)azanes; *X*-Ray Crystal and Molecular Structure of 2,4-Dipiperidino-1,3-di-t-butylcyclodiphosph(III)azane

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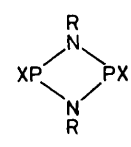
Summary Marked differences have been found in the nucleophilic reactivity, basicity, and photoelectron spectra of geometrical isomers of the cyclodiphosph(III)azanes, $(XPNBu^t)_2$ (X = NMe_2 or OMe), whose structures were assigned by reference to the crystal structure of *cis*-$(C_5H_{10}N{\cdot}PNBu^t)_2$.

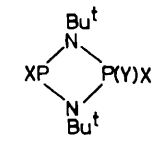
RECENTLY, considerable progress in the chemistry of the cyclodiphosph(III)azanes (I) has been achieved.[1-4]

The presence of geometrical isomers of (I) has been established by n.m.r. spectroscopy, but the isolation of both isomers has only once been reported.[5] Crystal structure determinations have usually been necessary to determine the configuration of individual isomers.[2,5-7] We now report on the crystal structure of a key amino-derivative, and show for the first time that geometrical isomers of (I) (R = Bu^t, X = NMe_2 or OMe) have remarkable differences in reactivity and physical properties, in addition to their very different ^{31}P shifts.[1]

Isomeric forms of (I) (R = Bu^t, X = NMe_2[1] or OMe) were separated by fractional crystallisation from pentane solution. Unexpectedly, the kinetically favoured higher melting dimethylamino-derivative has a *trans*-structure. This assignment is based on the crystal structure of the thermodynamically favoured *cis*-isomer of (I) (R = Bu^t, X = NC_5H_{10}) (NC_5H_{10} = piperidino), m.p. 97—98 °C, its properties in relation to those of isomeric forms of (I) (R = Bu^t, X = NMe_2), and the measurement of dipole moments (Table). Although there is a close parallel between the properties of isomeric dimethylamino- and methoxy-derivatives, the difference in dipole moments of the methoxy isomers is not great enough for a definite structural assignment.



(I)



(II)

X = NMe or OMe
Y = S, Se, or MeI

TABLE. Physical properties of cyclodiphosph(III)azanes

Compound (I) (R = Bu^t)	M.p./°C	δ_P[a]	μ/Debye[b]	$\Delta\nu$/cm^{-1} [c]	$\Delta\nu$/Hz[d]	Photoelectron spectrum eV[e]
X = NC_5H_{10}, *cis*	97—98	91·9[f]	2·8	28	22	7·5, 8·3, 8·7
X = NMe_2, *cis*	38—40	95·0	2·2	22	21	7·5, 8·2, 8·8
X = NMe_2, *trans*	114—116	184·7	0	42	42	7·1, 7·5, 8·5, 10·0
X = OMe	66 (0·1)[g]	133·7	2·1	10	17	8·4, 10·1
X = OMe	56—58	202·4	1·5	13	18	7·7, 8·3, 10·1

[a] $CDCl_3$ solutions, downfield relative to 85% H_3PO_4 (external). [b] In benzene solution, *trans*-isomers mixed with <*ca.* 10% *cis* isomer in solution. All ±0·5 D. [c] I.r. shift of ν (C–D) for $CDCl_3$ (0·04 M)/(I) (1 M) mixture in hexane, relative to pure $CDCl_3$. [d] ^1H n.m.r. chemical shift (60 MHz) of $CHCl_3$, 0·02 M in hexane relative to the same solution with added (I) (0·5 M). [e] Bands observed below 11 eV only. [f] *trans* isomer, δ_P 182·3, not isolated. [g] B.p./°C (*P*/mmHg); also reported by I. J. Colquhoun and W. McFarlane, *J.C.S. Dalton*, 1977, 1674.

An *X*-ray analysis of (I) (R = Bu^t, X = NC_5H_{10}), based on 3026 diffractometric intensities refined to $R = 0.045$, reveals that the molecular symmetry is almost exactly C_2 and that the piperidine rings are mutually *cis* with respect to the P_2N_2 ring (Figure). The *cis*-configuration leads to

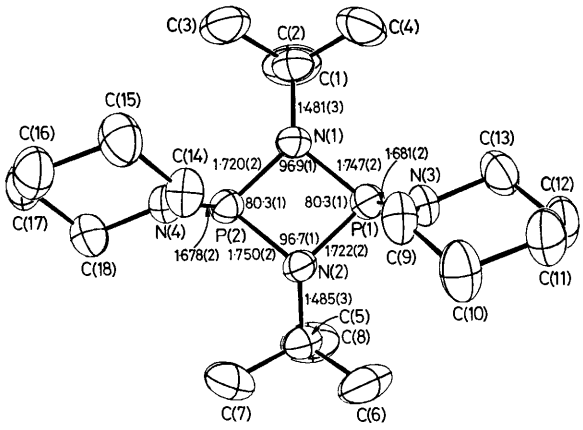


FIGURE. A view of the *cis*-(I) (R = Bu^t, X = NC_5H_{10}) molecule showing selected bond lengths (Å) and angles (°). Other values are: mean N–C(Bu^t) 1·483(2), mean N–CH_2 1·457(3)Å, N(1)–P(1)–N(3) 110·3(1), N(2)–P(1)–N(3) 105·3(1), N(1)–P(2)–N(4) 105·1(1), N(2)–P(2)–N(4) 109·3(1), P(1)–N(1)–C(1) 123·9(2), P(2)–N(1)–C(1) 125·8(2), P(1)–N(2)–C(5) 125·6(2), P(2)–N(2)–C(5) 123·8(2), C(9)–N(3)–C(13) 113·1(2), and C(14)–N(4)–C(18) 113·3(2)°.

cross-ring steric interactions between the piperidine substituents [C(9) · · · C(14) = 3·64 Å] which are relieved partly by opening of the P(1)–N(3)–C(9) and P(2)–N(4)–C(14) angles [respectively, 126·4(2) and 125·8(2)° compared with 118·2(2) and 118·6(2)° for P(1)–N(3)–C(13) and P(2)–N(4)–C(18)] and partly by twisting of the co-ordination planes of N(3) and N(4) so that they make dihedral angles of 100° with the mean P_2N_2 ring plane.† Whilst *trans*-cyclodiphosph(III)azanes contain planar P_2N_2 rings,[2,7] a very pronounced puckering of this ring is found here, successive atoms lying ±0·138 Å from the mean ring plane [*cf.* ±0·045 Å in *cis*-(I) (R = Bu^t, X = Cl)[6]]. A further novel feature of the P_2N_2 ring is the significant alternation of the P–N bond lengths. Indeed, the ring contains the longest P^{III}–N bonds so far observed.

In the reactions of a 1:1 mixture of isomers of (I) (R = Bu^t, X = NMe_2) (total, 1 mol equiv.) with elemental sulphur, selenium, or methyl iodide (0·5 mol equiv.) the formation of the mono-oxidation product (II) from the *trans*-isomer was essentially complete, leaving the unchanged *cis*-isomer. Closely related observations were made for reactions with the methoxy-derivatives [which gave Arbuzov-rearranged products, XP(NBu^t)P(O)Me(NBu^t) when Y = MeI]. These differences in nucleophilic reactivity are paralleled by the higher basicity of the *trans*-, relative to the *cis*-dimethylamino-derivatives, as measured by i.r.[8] and ^{1}H n.m.r.[9] studies of hydrogen bonding to $CDCl_3$ and $CHCl_3$, respectively (Table). The photoelectron spectra also reveal that the lowest energy bands are *ca.* 0·5 eV lower in binding energy in the *trans*-, relative to the *cis*-isomers (with the above-noted reservation on the structures of the methoxy-derivatives). The groups of bands quoted in the Table are the result of nitrogen–phosphorus (or oxygen–phosphorus) nonbonded electron-pair interactions and are difficult to assign.[10]

The formation of thermodynamically favoured *cis*-isomers by heating the *trans*-isomers of (I) (R = Bu^t, X = NMe_2, or NC_5H_{10}) is particularly intriguing in view of adverse steric effects in the former isomers. However, it is possible that destabilizing interactions between nitrogen and phosphorus lone pairs are reduced by twisting the cyclodiphosph(III)azane ring. Additionally, a cross ring $n_P \rightarrow \sigma^*_{P-N(or\ O)}$ bonding interaction, analogous to that which determines the relative stabilities of geometrical isomers of azo-compounds,[11] would be expected to stabilize the *cis*- relative to the *trans*-isomers. There is a marked contrast between the cyclodiphosph(III)azanes and cyclophosph(V)azenes,[12] where geometrical isomers of the latter compounds cannot be distinguished by basicity measurements and small differences in reactivity can only be indirectly inferred from observed reaction patterns.

We thank Dr. S. Cradock for obtaining the photoelectron spectra, Dr. C. J. Gilmore for help with computing, and Dr. J. K. Tyler for assistance with dipole moment measurements. The S.R.C. and the University of Glasgow are thanked for financial support.

(*Received, 24th January* 1978; *Com.* 071.)

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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