377. Phosphonitrilic Derivatives. Part XII.[1] The Heats of Polymerisation of the Cyclic Phosphonitrilic Chlorides

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The heats of polymerisation of the cyclic phosphonitrilic chlorides $(NPCl_2)_{3-7}$ have been determined by differential thermal analysis, and converted into heats of formation in the vapour phase by use of the known heat of formation of the trimeric chloride and appropriate vapour-pressure data. Stability increases steadily with ring size, as expected if the d_{xz}-orbital is the main contributor to the π-system, but more slowly than if it were the only factor. It is likely that geometrical restrictions on overlap in the medium-sized rings are also important.

In an earlier Paper,[2] the determination of the heats of formation of trimeric and tetrameric phosphonitrilic chlorides was described. The tetramer was found to be the more stable, but the difference between the heats of formation, in the vapour phase, of $NPCl_2$ monomer units in the two molecules was little greater than the uncertainties in the determined heats of combustion. In view of the interest in the energetics of potentially delocalised $p\pi$–$d\pi$ ring-systems, the relative heats of formation of the liquid phosphonitrilic chlorides have been determined more accurately, as far as the heptamer, by measuring their heats of polymerisation by differential thermal analysis. New vapour pressure results are presented for the tetramer to heptamer, and the derived heats of vaporisation are used to correct the heats of formation to the vapour-phase values.

Experimental

The preparation of the chlorides has been described elsewhere.[3] In the differential thermal analysis apparatus,[4] the sample to be studied (*ca.* 0·1 g., mixed with alumina) and the inert comparison material (alumina) were packed into thin-walled silica tubes which fitted closely into 7-mm. holes in a 1 in. diam. nickel block. The bases of the sample tubes were held in close contact with the twin, differentially connected thermocouple junctions,[5] which were of Pt/Pt–Rh (13%). The temperature of the nickel block was raised steadily by means of a vertical muffle furnace, the operation of which was controlled by a third thermocouple and a temperature-programming device. The temperature of the calorimeter and the differential output arising from thermal changes in the sample were displayed on a recording potentiometer, the constant rate of heating ensuring that the area of the peak was proportional to the heat change occurring in the sample.

The apparatus was calibrated by using the known heats associated with (1) the fusion of silver nitrate, (2) the fusion of benzoic acid, (3) the dehydration of calcium hydroxide, and (4) the decomposition of calcium carbonate. Calibrations 1 and 2 yielded sharp peaks, whereas calibrations 3 and 4 gave the flatter traces expected of time-dependent reactions. Similar broad peaks were obtained for the polymerisation reactions. Base-line drift was negligible, and the calibrations agreed amongst themselves to within ±3%, despite the different contours of the peaks employed. By using metallic zinc as a catalyst,[6] the heats of polymerisation could be determined conveniently in the temperature range 200—270° at a steady heating rate of about 3° per min. Concentrations of catalyst up to 2% by weight were used, the measured heats increasing slightly with concentration. The (linear) extrapolation to zero concentration of catalyst involved a correction of about 1% to the least measured heat for a particular compound. Benzoic acid also was an effective catalyst,[6] but gave erratic thermal results. In the absence of a catalyst, polymerisation was incomplete; the d.t.a. curves then showed endothermic peaks due to vaporisation of the cyclic chlorides. In the presence of catalyst, no

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[1] Part XI, A. C. Chapman and D. F. Carroll, *J.*, 1963, 5005.

[2] S. B. Hartley, N. L. Paddock, and H. T. Searle, *J.*, 1961, 430.

[3] L. G. Lund, N. L. Paddock, J. E. Proctor, and H. T. Searle, *J.*, 1960, 2542.

[4] W. J. Smothers and Y. Chiang, "Differential Thermal Analysis," Chemical Publishing Co., New York, 1958.

[5] J. A. Dunne and P. F. Kerr, *Amer. Min.*, 1960, **45**, 881.

[6] J. O. Konecny and C. M. Douglas, *J. Polymer Sci.*, 1959, **36**, 195.

endothermic peaks were observed. The test samples were inspected after every run; extraction of the rubber-like product with benzene gave no evidence of phosphonitrilic compounds of low molecular weight, and polymerisation was judged to be at least 96% complete in all cases. Results are given in Table 1; although no thermal effect could be detected with the heptamer, examination showed that polymerisation had taken place.

For the trimer, Steinman, Schirmer, and Audrieth's value [7] for ΔH_{vap} was accepted. The published data for the tetramer [8] are presented in the form of a graph, of approximate equation $\log_{10} p(\text{mm.}) = 8{\cdot}51 - (3360/T)$, from which $\Delta H_{\text{vap}} = 15{\cdot}4$ kcal./mole. In the present work, the results of which differ only slightly from those of Moureu and de Ficquelmont, vapour pressures were measured with an isoteniscope (using a glass spoon gauge to indicate equality of sample and balancing pressures), and by measurement of the boiling point at a series of pressures in the range 1—600 mm. The second method, though possibly less accurate, was used as a check, to ensure that the static readings had not been vitiated by partial polymerisation or decomposition. Similar methods were used for the pentamer and hexamer. A middle fraction of the pentamer was distilled into the apparatus, and degassed at 10^{-6} mm. before making measurements. The values obtained were continuous with those found by determination of the boiling point at temperatures above 300°. The directly-measured boiling point of $(NPCl_2)_5$ was found to be 371·5°/760 mm. The vapour pressures of the heptamer were measured only by boiling point and are comparatively inaccurate. The heats of vaporisation of the cyclic chlorides are expressible by the formula $\Delta H_{\text{vap}} = 5{\cdot}6 + 2{\cdot}5n \pm 0{\cdot}2$ kcal./mole, up to $(NPCl_2)_7$.

TABLE 1

Thermal quantities for phosphonitrilic chlorides

	Vapour pressure data *				ΔH_{pol} (kcal./mole) †	
n in $(NPCl_2)_n$	A	B	ΔH_{vap} (kcal./mole)	Temp. range	$-\Delta H_{\text{lc}}$	$-\Delta H_{\text{gc}}$
3	8·357	2880	13·2 ± 0·1	114—189°	1·39 ± 0·12	14·59 ± 0·16
4	8·498	3358	15·35 ± 0·1	123—306	0·86 ± 0·06	16·21 ± 0·13
5	9·10	3973	18·15 ± 0·15	170—371	0·80 ± 0·06	18·95 ± 0·17
6	9·576	4533	20·7 ± 0·2	205—349	0·26 ± 0·04	20·96 ± 0·2
7	10	5060	23·1 ± 0·5	226—305	0 ± 0·05	23·1 ± 0·5
∞	—	—	2·5 ‡	—	0	2·5 — 3·3 §

* $\log_{10} p$ (mm.) $= A - (B/T)$; the probable errors in ΔH_{vap} were estimated graphically. † ΔH_{lc} and ΔH_{gc} stand for heats of polymerisation from liquids to condensed phase, and from gas to condensed phase, respectively. The errors quoted are a combination of root-mean-square derivations in repeated thermal experiments, the uncertainty of the correction for incomplete polymerisation, and (in the last column) the probable errors in the heats of polymerisation. Possible errors in the calibration have been ignored. ‡ Extrapolated value per $NPCl_2$ unit. § This represents the heat of condensation of a single $NPCl_2$ unit in the high polymer. The lower figure is obtained from the incremental value of ΔH_{vap} given; inclusion of an additional 0·8 kcal./$NPCl_2$ unit, of the same order as the heats of fusion of this unit in the lower cyclic chlorides (Oldfield, unpublished), but possibly here an overestimate, leads to the upper figure.

DISCUSSION

The results show that polymerisation of the ring compounds is exothermic, but decreasingly so for increasing molecular weight. The conversion of the heats of polymerisation into relative heats of formation requires the assumption that each cyclic chloride forms the same high polymer. Though this has not yet been proved, the authors of a Paper [9] on the structure of a polyphosphonitrilic chloride (referred to in more detail below) stress the differences from the structure of the trimer from which it was made; the structure of the high polymer will be assumed here to be independent of its source. On this basis, the heat of formation of a monomer unit in each of the cyclic oligomers in the gas phase increases steadily, within experimental error, at least up to the heptamer (see Figure). In particular, the increased heat of formation of the tetramer relative to the trimer can be seen to be real, and greater than was found in the combustion experiments. It is possible also to make

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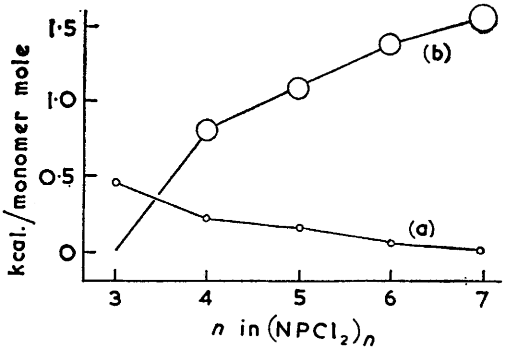
[7] R. Steinman, F. B. Schirmer, and L. F. Audrieth, *J. Amer. Chem. Soc.*, 1942, **64**, 2377.

[8] H. Moureu and A. M. de Ficquelmont, *Compt. rend.*, 1941, **213**, 306.

[9] E. Giglio, F. Pompa, and A. Ripamonti, *J. Polymer Sci.*, 1962, **59**, 293.

an estimate of the heat of sublimation of the high polymer, by using the incremental heat of vaporisation determined for the first few cyclic compounds, and hence relate its heat of formation, too, to that of the trimer. Expressed as for the cyclic compounds (Figure b) $[\Delta H_f(NPCl_2)$ (in trimer) (g) $- \Delta H_f(NPCl_2)$ (in high polymer) (g)$] = 1{\cdot}56$ kcal./mole, if an estimated heat of fusion is included (see Table 1, note §).

The P–N and P–Cl bonds joining at a phosphorus atom interact with one another, so that changes in both must contribute to the changes in heat of formation. However, the biggest single change in energy (from trimer to tetramer) is accompanied by a change in Cl–P–Cl angle from 101·9° (average)[10] in $(NPCl_2)_3$ to only 102·8° in $(NPCl_2)_4$ (K-form),[11] a difference which barely exceeds the standard deviation of the separate angles. The changes in σ-bond energy are evidently small, and in any case the cyclic and exocyclic changes would tend to compensate one another. We shall assume here that the whole energy variation is to be attributed to the ring π-bonds.



(a) $-\Delta H_{1c}$ for a single $NPCl_2$ unit in each cyclic chloride up to $(NPCl_2)_7$.
(b) Relative negative heats of formation of the same unit; $\Delta H_f(NPCl_2)$(in trimer)(g) $-$ $\Delta H_f(NPCl_2)$(in *n*-mer)(g).
(The radii of the circles on the upper curve represent probable error.)

In *p*π–*d*π systems, two bond systems which change orbital signs on reflection in a local bond direction have been distinguished[12,13] and, for cyclic systems, labelled as π- and π′-bonding,[12] the latter involving the in-plane *d*-orbitals, $d_{x^2-y^2}$ and d_{xy}. The structural evidence, mainly on the configuration of 8-membered rings, has been interpreted[12] as showing π-bonding to be more important than π′-bonding in the cases of interest. This estimate of relative importance is confirmed by a study of the high polymer,[9] which has a *cis*-planar structure which at the same time maximises *p*π–*d*π overlap and minimises the mutual repulsion of non-bonded groups. Features of the geometry of three phosphonitrilic chloride structures are summarised in Table 2. The average deviation from parallelism of the π-orbital axes at successive ring atoms decreases from 36·4° in the tetramer to 19° in the high polymer, with consequent improvement of π-overlap. The π′-system in the high polymer depends almost wholly on the delocalisation of the lone pair at nitrogen, and

TABLE 2

Molecular geometry of phosphonitrilic chlorides

	Average ring bond length P–N (Å)	Average bond angles NPN	PNP	Torsion angles *	Ref.
$(NPCl_2)_3$	1·59	119·6°	120°	0°	10
$(NPCl_2)_4$	1·58	121·2	132	15° 34′, 57° 18′	11
$(NPCl_2)_\infty$	1·60	119	127	14°, 24°	9

* Angles between the normals to successive PNP, NPN planes, and hence between the axes of the π-orbitals at successive ring atoms.

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[10] A. Wilson and D. F. Carroll, *J.*, 1960, 2548; F. Pompa and A. Ripamonti, *Ricerca sci.*, 1959, **29**, 1516.
[11] R. Hazekamp, T. Migchelsen, and A. Vos, *Acta Cryst.*, 1962, **15**, 539.
[12] D. P. Craig and N. L. Paddock, *J.*, 1962, 4118.
[13] D. W. J. Cruickshank, *J.*, 1961, 5486.

is therefore weaker than the π-system. If, on the simplest view, π'-bonding is ignored, and if, also, the two $d\pi$-orbitals (d_{xz} and d_{yz}) participate equally,[14] the heat of formation of an $NPCl_2$ unit should be almost independent of ring size. However, the site symmetry at phosphorus, at most C_{2v}, does not require this equality. The different d_{xz}–$p\pi$ and d_{yz}–$p\pi$ overlaps, allowance being made for unequal polarisation of the d-orbitals by the nitrogen and chlorine atoms,[15] ensure that d_{xz} is the more important π-orbital, and, in this case, the π-electron energy (per electron) increases to a limit with increasing ring size, as found, though the variation is less rapid than expected on the simplest theoretical basis.[16]

Other factors contribute to the heats of formation, but cannot account for all the facts. First, the angle at nitrogen is smaller in the trimer than in the tetramer and high polymer, and, if the natural angle is that found in the geometrically unconstrained tetramer molecule, the trimer might be considered to be destabilised by steric strain. If this strain were of major importance, the ring angle at phosphorus should also be reduced in the trimer, whereas these angles are nearly equal in all phosphonitrilic compounds of known structure, and are of the order expected for strain-free bonds. Also, since such geometrical constraint occurs only in the six-membered ring, it is impossible to account in this way for the further increases in heat of formation found for molecules larger than the tetramer. Secondly, the large angles at nitrogen in both the tetramer and the high polymer indicate some contribution to the bonding from the delocalisation of lone pairs on the nitrogen atoms. Insofar as the π-orbitals of phosphorus are thereby occupied, the qualitative dependence of the energies on ring size remains unaltered, the effect being to reduce (but not to eliminate) the dependence of delocalisation energy on molecular configuration. So long as the torsion angles do not exceed 45°, the main contribution of the lone pairs is to π'-bonding. Use of the d_{xy}-orbital reinforces the variation expected from d_{xz}, since the symmetries of their interactions with the relevant orbitals on adjacent atoms are the same. The $d_{x^2-y^2}$ orbital on the other hand, should interact more strongly[15] than d_{xy}, and, because it interacts symmetrically with s–p-hybrids on adjacent atoms,[12] should stabilise especially the odd-numbered polymers; if strong enough, it could destabilise the tetramer relative to the trimer. Since no such alteration is observed, it is probable that π'-bonding, although important stereochemically,[12] has a smaller effect on bond energies. Finally, because of the closer approach to local planarity possible in the larger rings, increase of molecular size above the tetramer leads to improved orbital overlap. This factor is probably important, but cannot be the sole cause of the variation of energy with ring size, because, if it were, the trimer would be a little less stable than the high polymer, and the tetramer less stable than both. On a smaller scale, its effect would be to destabilise the tetramer, and (decreasingly) the larger molecules. The experimental heats of formation can therefore be understood as arising from $p\pi$–$d\pi$ bonding, using principally the d_{xz}-orbital of phosphorus, but with some contribution from the other factors mentioned. The variation of the heats with ring size is, however, less rapid than expected from calculations on the simple model of D_{nh} symmetry; we attribute the difference mainly to geometrical restrictions on orbital overlap in the medium ring sizes.

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[14] M. J. Dewar, E. A. C. Lucken, and M. A. Whitehead, *J.*, 1960, 2423.

[15] K. A. R. Mitchell, quoted in ref. 12, and Thesis, London, 1963.

[16] D. P. Craig, *J.*, 1959, 997; D. P. Craig and N. L. Paddock, *Nature*, 1958, **181**, 1052.