898. *Heats of Formation and Bond Energies.   Part IV.* Hexacyclo-hexyloxycyclotriphosphazatriene,   Hexamethylcyclotriphosphazatriene, and Octaphenylcyclotetraphosphazatetraene.*

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Values are reported for the heats of combustion of hexacyclohexyloxy-cyclotriphosphazatriene, $\Delta H_c^\circ\{[\mathrm{PN(C_6H_{11}O)_2}]_3$, c$\} = -5669\cdot6 \pm 4\cdot0$; hexa-methylcyclotriphosphazatriene, $\Delta H_c^\circ[(\mathrm{PNMe_2})_3$, c$] = -1665\cdot1 \pm 2\cdot7$; octa-phenylcyclotetraphosphazatetraene, $\Delta H_c^\circ[(\mathrm{PNPh_2})_4$, c$] = -6736\cdot5 \pm 11\cdot5$ kcal./mole, to crystalline orthophosphoric acid, liquid water, and gaseous carbon dioxide. These data are used to calculate the heats of formation of the crystalline compounds as $-582\cdot0 \pm 4\cdot0$; $-125\cdot1 \pm 2\cdot7$; and $40\cdot7 \pm 11\cdot5$ kcal./mole.

Comment is made on the variation of the P–N bond energies in the ring system, and also of the P–R bond energies in the compounds $(\mathrm{PNR_2})_{3\,\mathrm{or}\,4}$.

THE aromatic character of the cyclic phosphazenes (I and II) has been pointed out by Craig and Paddock.[1] Whilst the chloro-compounds $(\mathrm{PNCl_2})_3$ and $(\mathrm{PNCl_2})_4$ have been known for many years, compounds in which the groups R are less electronegative have been prepared only recently. In 1958 Haber[2] reported the preparation of pure octa-phenylcyclotetraphosphazatetraene (II; R = Ph) and in 1959 hexamethylcyclotri-phosphazatriene (I; R = Me) was prepared by Searle.[3] With these, compounds have now been obtained in which R contains the group –C≡, –N=, –O–, or halogen and it is of

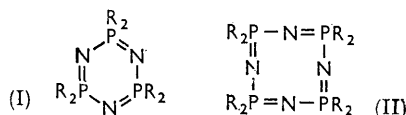* Part III, *J.*, 1960, 3284.

[1] Craig and Paddock, *Nature*, 1958, **181**, 1052; Craig, *Chem. and Ind.*, 1958, 3.
[2] Haber, Herring, and Lawton, *J. Amer. Chem. Soc.*, 1958, **80**, 2116.
[3] Searle, *Proc. Chem. Soc.*, 1959, 7.

interest to know how the bonding in these molecules is affected by change in electro-negativity of the group R.

As a beginning, the heats of formation have been determined of the methyl (I; R = Me)

and phenyl (II; R = Ph) compounds and also of hexacyclohexyloxycyclotriphosphaza-triene (I; R = cyclo-$C_6H_{11}O$) to supplement data which already exist [4] for hexachloro-cyclotriphosphazatriene (I; R = Cl). It is hoped later to present heats of formation of the hexafluoro- (I; R = F) and hexadimethylamino-cyclotriphosphazatriene (I; R = NMe_2).

The hexacyclohexyloxy-derivative was chosen because it tends not to undergo the elimination reactions of the hexaethoxy-compound: [4]
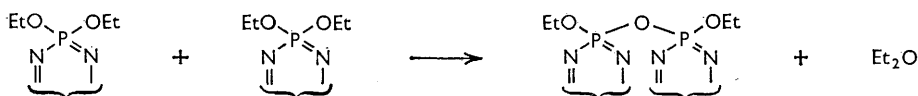
EXPERIMENTAL

Materials.—Octaphenylcyclotetraphosphazatetraene was supplied by Dr. C. P. Haber of the U.S. Naval Ordnance Laboratory, Corona, California, U.S.A. It had been prepared [2] from trichlorodiphenylphosphorane and ammonia. After being dried (P_2O_5) it had m. p. 319·5—321·0°. Hexamethylcyclotriphosphazatriene and hexacyclohexyloxycyclotriphosphaza-triene were given by Albright and Wilson (Mfg.) Ltd. The hexamethyl compound, m. p. 195—196°, had been prepared [3] from trichlorodimethylphosphorane and ammonium chloride and the hexacyclohexyloxy-derivative, m. p. 184·0°, from hexachlorocyclotriphosphazatriene and sodium cyclohexoxide.

Combustion Calorimetry.—Combustions were made in a twin-valve bomb (Parr Instrument Co., Moline, Illinois, U.S.A.) which together with the subsidiary apparatus has been described previously.[5] The solid phosphazenes were compressed into pellets. The bomb was charged with oxygen at an initial pressure of 30 atm. and with 3 ml. of water. Each sample was fired at 25°.

All combustions were initiated by a platinum wire and cotton fuse. This was sufficient to cause almost complete combustion of the cyclohexyloxy-compound, but with the other derivatives only partial burning resulted. Additional fuses of benzoic acid for the phenyl compound and Melinex for the methyl compound were used.

The temperature of combustion of the phenyl compound was sufficiently high to damage the platinum crucible; because of the possible reaction between platinum and phosphate ions, at these temperatures, a silica crucible was used.

In the combustion of phosphorus compounds containing hydrogen, the phosphorus pentoxide dissolves in the water simultaneously produced, to form phosphoric acid. At high concen-trations of acid the heat of dilution is considerable, and thermochemical errors due to inhomo-geneity of the liquid phase would be large. The procedure suggested by Long and Sackman [6] was adopted to minimise these errors. For this reason the bomb was charged with more water (3 ml.) than is customary (1 ml.), so as to give an N-solution of phosphoric acid. Part of this water was condensed on the interior walls and underside of the bomb head by placing the bomb in a warm-water bath.

Analysis.—After combustions the gases from the bomb were analysed for carbon dioxide to an accuracy of ±0·02%. The remainder of the bomb contents was filtered and the solid residue, which appeared to be unburnt compound and carbon in the case of the phenyl and methyl compounds, was dried and weighed. This residue was digested with benzene, in which

[4] Paddock and Searle, *Adv. Inorg. Chem. and Radiochem.*, 1959, **1**, 347.
[5] Fletcher, Mortimer, and Springall, *J.*, 1959, 580.
[6] Long and Sackman, *Trans. Faraday Soc.*, 1957, **53**, 1606.

these derivatives are soluble, dried, and re-weighed. In this way the weights of unburnt compound and carbon were found. This weight of unburnt compound recovered was usually about 0·2% less than calculated from the initial weight of sample, of carbon dioxide, and of carbon.

A part of the bomb-washings was titrated with 0·1n-sodium hydroxide solution, thymolphthalein being used as indicator, to give the total phosphorus acid and nitric acid. A second part was treated with acetic acid, hydrochloric acid, and mercuric chloride. In no case was mercurous chloride precipitated, showing the absence of phosphorous acids. A third part was analysed for orthophosphoric acid by the quinoline–phosphomolybdate method [7] to an accuracy of ±0·1%. A fourth part was boiled with nitric acid to convert condensed acids into the ortho-acids, and the total phosphoric acids found. In no case was any condensed phosphoric acid found. The quantity of phosphate recovered corresponded to within ±0·2% with the amount formed, as calculated from the recovery of carbon, carbon dioxide, and unburnt compound.

Units and Auxiliary Quantities.—The heats of combustion are given in units of the thermochemical calorie, 1 cal. = 4·1840 abs. j. The energy equivalent of the calorimeter was determined by combustion of a sample of benzoic acid having $-\Delta U_b = 6·3181 \pm 0·0007$ cal./g. The heats evolved in the following processes were taken to have the values given; (a) the formation of 0·1n-nitric acid from nitrogen, oxygen, and water, 13·81 kcal./mole,[8] (b) the combustion of cotton fuse, 3·88 kcal./g.; [9] (c) the combustion of Melinex, 1052·9 kcal./mole, i.e., $(C_{10}H_4O_4)_n/n$; [10] (d) the solution of crystalline phosphoric acid to give a 1·0n-solution, 2·9 kcal./mole; [11] (e) the combustion of carbon (soot) to carbon dioxide, 8·11 kcal./g.

Results.—The results of the combustions are given in Tables 1—3, in which the symbols have the same meaning as in Part II of this series.[12] In addition, the following terms are used here: q_b = heat of combustion of benzoic acid, q_m = heat of combustion of Melinex fuse; CO_2 obs. : calc. = the ratio of the carbon dioxide recovered and that equivalent to unburnt carbon, to the carbon dioxide calculated for complete combustion of the phosphazene sample.

The mass of sample burnt in each experiment was calculated from the mass of carbon dioxide and carbon formed (uncertainty ± 0·02%), the cotton fuse, benzoic acid, or Melinex fuse being assumed to have been burnt completely. This mass was also found, though slightly less accurately, from analysis for orthophosphoric acid (uncertainty ± 0·1%), or from recovery of unburnt compound (uncertainty ± 0·2%).
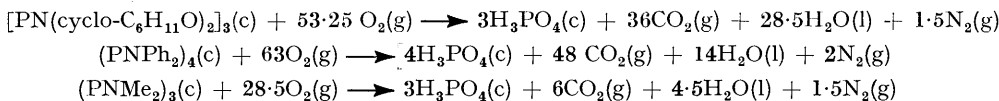
The $\Delta H_c°$ values refer to the reactions:

$$[PN(cyclo\text{-}C_6H_{11}O)_2]_3(c) + 53·25\ O_2(g) \longrightarrow 3H_3PO_4(c) + 36CO_2(g) + 28·5H_2O(l) + 1·5N_2(g)$$

$$(PNPh_2)_4(c) + 63O_2(g) \longrightarrow 4H_3PO_4(c) + 48\ CO_2(g) + 14H_2O(l) + 2N_2(g)$$

$$(PNMe_2)_3(c) + 28·5O_2(g) \longrightarrow 3H_3PO_4(c) + 6CO_2(g) + 4·5H_2O(l) + 1·5N_2(g)$$

TABLE 1. *Hexacyclohexyloxycyclotriphosphazatriene* (M 729·837).

Expt.	1	2	3	4
Wt.* sample (g.)	0·514735	0·432819	0·470592	0·505569
ΔR_c (ohm)	0·10004	0·08436	0·09137	0·09864
CO_2 obs. : calc. (%)	99·73	99·92	99·68	99·85
q_i (cal.)	6·8	5·6	5·4	4·9
q_n (cal.)	6·4	6·1	6·2	6·3
q_p (cal.)	2·8	2·4	2·6	2·8
q_w (cal.)	0·9	0·7	0·8	0·8
E_c (cal./ohm)	7·3	6·1	6·6	7·1
$-\Delta U_c°$ (kcal./mole)	5656·2	5660·7	5654·2	5669·9

$-\Delta U_c°$ mean value, 5660·2 kcal./mole (standard deviation of mean ±3·5 kcal./mole).
$E_s = 39944·6$ cal./ohm: $\bar{s}E = \pm 0·04\%$.
$\bar{s}\Delta U_c° = \pm 0·06\%$: $\bar{s} = \pm 0·07\%$: $\Delta nRT = -9·39$ kcal./mole: $-\Delta H_c° = 5669·6 \pm 4·0$ kcal./mole.

* All weights *in vacuo.*

[7] Wilson, *Analyst.*, 1951, **76**, 55.
[8] Prosen, " Experimental Thermochemistry," Interscience, New York, 1956, Ch. 6.
[9] Coops, Jessup, and van Nes, *op. cit.*, Ch. 3.
[10] Evans and Skinner, *Trans. Faraday Soc.*, 1959, **55**, 256.
[11] National Bureau of Standards Circular 500, Washington, D.C., 1952.
[12] Bedford and Mortimer, *J.*, 1960, 1622.

TABLE 2. *Hexamethylcyclotriphosphazatriene* $(M, 225 \cdot 123)$.

Expt.	1	2	3
Wt.* sample (g.)	0·30731	0·33710	0·27016
ΔR_c (ohm)	0·06983	0·07735	0·06445
CO_2 obs. : calc. (%)	95·71	99·05	—
Wt. carbon (g.)	0·0006	0·0014	0·0080
q_m (cal.)	690·6	598·3	576·4
q_i (cal.)	4·8	4·7	4·8
q_n (cal.)	1·0	13·2	3·2
$-q_c$ (cal.)	4·9	11·4	6·4
q_p (cal.)	10·9	12·8	10·3
q_w (cal.)	0·1	0·1	0·1
E_c (cal./ohm)	0·5	0·6	0·5
$-\Delta U_c^\circ$ (kcal./mole)	1656·2	1662·5	1664·5

$-\Delta U_c^\circ$ mean value $= 1661 \cdot 0$ kcal./mole (standard deviation of mean $\pm 2 \cdot 7$ kcal./mole).
$E_s = 40,120 \cdot 0$ cal./ohm: $\bar{s}E = \pm 0 \cdot 04\%$.
$\bar{s}\Delta U_c^\circ = \pm 0 \cdot 15\%$: $\bar{s} = \pm 0 \cdot 16\%$: $\Delta nRT = 4 \cdot 1$ kcal./mole: $-\Delta H_c^\circ = 1665 \cdot 1 \pm 2 \cdot 7$ kcal./mole.

TABLE 3. *Octaphenylcyclotetraphosphazatetraene* $(M, 796 \cdot 732)$.

Expt.	1	2	3	4	5
Wt.* sample (g.)	0·400837	0·648472	0·574319	0·668321	0·565544
ΔR_c (ohm)	0·11390	0·16448	0·13353	0·15755	0·13415
CO_2 obs. : calc. (%)	98·81	99·82	98·73	99·40	99·34
Wt. carbon (g.)	0·00863	0·00100	0·00305	0·00552	0·00458
q_b (cal.)	1275·6	1126·7	627·5	715·2	679·2
q_i (cal.)	9·5	8·9	6·2	6·5	6·2
q_n (cal.)	3·6	15·0	17·3	20·3	16·2
$-q_c$ (cal.)	70·0	8·1	24·7	44·8	37·1
q_p (cal.)	5·6	9·0	7·9	9·3	7·9
q_w (cal.)	1·5	2·6	2·2	2·7	2·1
E_c (cal./ohm)	5·2	8·4	7·4	8·6	7·3
$-\Delta U_c^\circ$ (kcal./mole)	6737·6	6738·7	6705·0	6761·9	6700·9

$-\Delta U_c^\circ$ mean value $= 6728 \cdot 8$ kcal./mole (standard deviation of mean $= \pm 11 \cdot 5$ kcal./mole).
$E_s = 40,120 \cdot 0$ cal./ohm. $\bar{s}E = \pm 0 \cdot 04\%$.
$\bar{s}\Delta U_c^\circ = \pm 0 \cdot 19\%$: $\bar{s} = \pm 0 \cdot 19\%$: $\Delta nRT = -7 \cdot 7$ kcal./mole: $-\Delta H_c^\circ = 6736 \cdot 5 \pm 11 \cdot 5$ kcal. mole.

Although the uncertainty associated with the heat of combustion of the phenyl compound of high molecular weight is large ($\pm 11 \cdot 5$ kcal./mole), this and the other uncertainties are comparatively small percentage deviations, the largest being $\pm 0 \cdot 2\%$.

Using the ΔH_f° values: $H_2O(l) - 68 \cdot 3174$; $CO_2(g) - 94 \cdot 0518$; and $H_3PO(c) - 306 \cdot 2$ kcal./mole,[11] we have calculated the heats of formation $\Delta H_f^\circ\{[PN(cyclo-C_6H_{11}O)_2]_3,c\} = -582 \cdot 0 \pm 4 \cdot 0$; $\Delta H_f^\circ[(PNPh_2)_4,c] = 40 \cdot 7 \pm 11 \cdot 5$; and $\Delta H_f^\circ[(PNMe_2)_3,c] = -125 \cdot 1 \pm 2 \cdot 7$ kcal./mole. The heats of sublimation of these compounds have not been measured but are estimated as 18 ± 2 kcal./mole. These lead to heats of formation of the gaseous compounds of $-564 \cdot 0 \pm 4 \cdot 0$, 58 ± 13, and -107 ± 5 kcal./mole, respectively.

DISCUSSION

The thermochemistry of the cyclic phosphazenes is best interpreted in terms of bond energies, and the first step in deriving these quantities is to calculate the heats of formation of the gaseous compounds from the atoms, ΔH_f^a (g), given by

$$\Delta H_f^a (g) = \Delta H_f^\circ (g) - \Delta H_a,$$

where the ΔH_a terms are the heats of atomisation of the elements. Values used are: C, $170 \cdot 89$; H, $52 \cdot 09$; O, $59 \cdot 54$; N, $112 \cdot 9$; P, $75 \cdot 3$; and Cl, $28 \cdot 94$ kcal./g.-atom.[13] From these ΔH_f^a (g) values the sum of the bond energies in the " ring unit," $E(N-PR_2-N)$, is derived. This is one third (for trimeric compounds) or one quarter (for the tetrameric compound) of the ΔH_f^a (g) terms. The problem then arises how to divide this energy amongst the bonds in the ring unit.

[13] Cottrell, " The Strengths of Chemical Bonds," Butterworths, 2nd Edn., London, 1958.

The structure of the trimeric chloride has been investigated by Brockway and Bright,[14] by electron diffraction, and by Wilson,[15] by X-rays. In both cases the structure suggested is one in which each phosphorus atom carries two chlorine atoms in a plane perpendicular

TABLE 4.   *Bond energies in cyclic phosphazenes (in kcal./mole).*

Compound	ΔH_f° (g.)	$E(\text{N--PR}_2\text{--N})$	$E(\text{P--R})$ in $(\text{PNR}_2)_n$	$E(\text{P--R})$ in PR_3	ΔE $\text{PR}_3/(\text{PNR}_2)_n$	ΔE PR_3/OPR_3	Ref.
$(\text{PNCl}_2)_3$	$-178\cdot1$	$305\cdot4$	$80\cdot3$ [a]	$76\cdot2$	$4\cdot1$	$4\cdot1$	18
$[\text{PN}(\text{OC}_6\text{H}_{11})_2]_3$	$-565\cdot0$	$3757\cdot7$	$135\cdot3$ [a]	$92\cdot0$	$43\cdot3$	$11\cdot0$	(c)
$(\text{PNMe}_2)_3$.........	$-107\cdot1$	$878\cdot3$	$68\cdot3$ [a]	$61\cdot6$	$6\cdot7$	$8\cdot1$	6, 24
$(\text{PNPh}_2)_4$	$+58\cdot7$	$2745\cdot1$	$80\cdot5$ [b]	$67\cdot5$	$13\cdot0$	$4\cdot5$	12, 25

Notes (a) based on $E(\text{N--P--N}) = 144\cdot8$ kcal./mole. *(b)* based on $E(\text{N--P--N}) = 146$ kcal./mole. *(c)* as found for $\text{PO}(\text{OEt})_3$ and $\text{PO}(\text{OPr}^i)_3$, ref. 12 and 25.

to the P_3N_3 ring. From electron diffraction the bond lengths are P–N, $1\cdot65 \pm 0\cdot03$ Å, and P–Cl, $1\cdot97 \pm 0\cdot03$ Å; from X-ray measurements the bond lengths are P–N, $1\cdot61 \pm 0\cdot04$ Å, and P–Cl, $1\cdot99 \pm 0\cdot04$ Å. Although there is a slight difference in the P–N length, as determined by the two methods, the two values lie within the experimental errors, and the P–N bond length is considerably shorter than the value of $1\cdot78$ Å found for the P–N single bond is sodium phosphoramidate.[16] The length of the P–Cl bond, by either method, lies closer to the value of $1\cdot99$ Å found in phosphoryl chloride, than to $2\cdot04$ Å found in phosphorus trichloride.[17] On this it seems reasonable to assume that the bond energy of the P–Cl bond in $(\text{PNCl}_2)_3$ is similar to that in phosphoryl chloride, and we take $E(\text{P--Cl}) = 80\cdot3$ kcal./mole.[18] From the relation

$$E(\text{N--PR}_2\text{--N}) = 2E(\text{P--R}) + E(\text{N--P--N}),$$

this gives $E(\text{N--P--N}) = 144\cdot8$ kcal./mole.

If the stretching frequency of the P–N bond, in the ring system, can be taken as a measure of its strength, then the values in Table 5 indicate that for the six-membered ring

TABLE 5.   *Stretching frequencies of P–N ring bond in cyclic phosphazenes.*

Compound	P–N Frequency (cm.$^{-1}$)	Ref.	Compound	P–N Frequency (cm.$^{-1}$)	Ref.
$(\text{PNF}_2)_3$	1297	19	$(\text{PNF}_2)_3$	1297	19
$[\text{PN}(\text{OMe})_2]_3$	1242	19	$(\text{PNCl}_2)_3$	1218	19
$[\text{PN}(\text{NMe}_2)_2]_3$ ...	1195	20	$(\text{PNBr}_2)_3$	1175	19
$(\text{PNMe}_2)_3$	1180	19			

systems there is a regular decrease in the bond-energy term $E(\text{N--P--N})$ along the series $\text{R} = -\text{O--}, -\text{Cl}, -\text{N=}, -\text{C}\equiv$. Hence the value found for $E(\text{N--P--N})$ in $(\text{PNCl}_2)_3$ can be taken as a maximum for the compounds in which $\text{R} = -\text{C}\equiv$• The value $E(\text{N--P--N}) = 144\cdot8$ kcal./mole gives minimum values for the bond energies $E(\text{P--R})$, which are shown in Table 4. These are obtained by incorporating bond-energy terms for the R groups. Values used are $E(\text{cyclo-C}_6\text{H}_{11}\text{O}) = 1671\cdot1$ kcal./mole, derived from ΔH_f° (cyclo-$\text{C}_6\text{H}_{11}\text{OH}$, l) $= -83\cdot45$ kcal./mole,[21] $\Delta H_{\text{vap}} = 11\cdot7$ kcal./mole,[22] and $E(\text{O--H}) = 110\cdot6$ kcal./mole;[13] $E(\text{Me}) = 298\cdot4$ and $E(\text{Ph}) = 1219\cdot4$ kcal./mole, derived from heats of formation given in ref. 11 and 26, and $E(\text{C--H}) = 98\cdot7$ kcal./mole.[13]

It is uncertain to what extent the P–N bonds in the ring system are stronger in $[\text{PN}(\text{OC}_6\text{H}_{11})_2]_3$ than in $(\text{PNCl}_2)_3$. However, $E(\text{N--P--N})$ again being taken as $144\cdot8$ kcal./mole, then $E(\text{P--O}) = 135\cdot3$ kcal./mole, in this case a maximum value.

[14] Brockway and Bright, *J. Amer. Chem. Soc.*, 1943, **65**, 1551.
[15] Wilson, see ref. 4, p. 366.
[16] Hobbs, Corbridge, and Raistrick, *Acta. Cryst.*, 1953, **6**, 621.
[17] Sutton, *Chem. Soc. Special Publ. No. 11*, 1958.
[18] Fowell and Mortimer, *J.*, 1959, 2913.
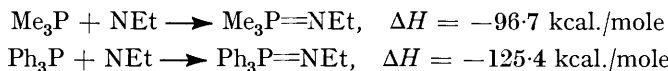[19] Searle, personal communication, 1959.
[20] Shaw, *Chem. and Ind.*, 1959, 54.
[21] Newitt and Schmidt, *J.*, 1937, 1665.
[22] Richards and Davies, *J. Amer. Chem. Soc.*, 1920, **42**. 1599.

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For the compound $(PNPh_2)_4$, there is the added uncertainty of the effect of increased ring size on the bond-energy term $E(N-P-N)$. Paddock [23] has found that $E(N-P-N)$ in $(PNCl_2)_4$ is greater, by some 1·6 kcal./mole, than in $(PNCl_2)_3$, and if a similar difference exists in the compounds $(PNPh_2)_3$ and $(PNPh_2)_4$, then we may use the value $E(N-P-N) = 146$ kcal./mole for $(PNPh_2)_4$, as a maximum value to derive a minimum value for $E(P-C)$ in this compound.

In Table 4 the corresponding bond energies for the tervalent phosphorus compounds PR_3, are shown, and the difference, ΔE, between these values and those found in $(PNR_2)_n$ compounds. These differences are considerably greater than those between the compounds PR_3 and POR_3, also given for comparison. Support for two of the ΔE values, where $R = Me$ and Ph, comes from a determination of the heats of the gas-phase oxidations [24]

$$Me_3P + NEt \longrightarrow Me_3P{=}NEt, \quad \Delta H = -96\cdot7 \text{ kcal./mole}$$

$$Ph_3P + NEt \longrightarrow Ph_3P{=}NEt, \quad \Delta H = -125\cdot4 \text{ kcal./mole}$$

If it is assumed that the bond energy of the group $P{=}NEt$ is the same in both cases, then on oxidation, each of the $P-Ph$ bonds is strengthened to an extent of some 9·6 kcal./mole more than the strengthening of the $P-Me$ bonds. A difference of 6·3 kcal./mole in the same sense is found between the ΔE values derived from the cyclophosphazene compounds.

The group energy $E(N-P-N) = 144\cdot8$ kcal./mole gives $E(P-N) = 72\cdot4$ kcal./mole, in the ring system, for $(PNCl_2)_3$. This is some 5·6 kcal./mole stronger than $E(P-N)$ in the tervalent phosphorus compound $P(NEt_2)_3$.[18] However, in the absence of a suitable " standard " of bond energies against which $E(P-N)$ in the cyclic phosphazenes can be properly compared, it is difficult to calculate a " resonance " energy of the system.

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      Keele, Staffs.

[23] Paddock, personal communication, 1959.
[24] Claydon, Fowell, and Mortimer, *J.*, 1960, 3284.
[25] Chernick, Skinner, and Mortimer, *J.*, 1955, 3936; Neale and Williams, *J.*, 1952, 4535; 1954, 2156.
[26] American Petroleum Institute Reseach Project 44, Carnegie Press, Pittsburg, Pa., 1953.