Chlorine-35 Nuclear Quadrupole Resonance Studies of Some Six-membered Ring Systems containing Nitrogen, Sulphur, and/or Phosphorus: α-$(NSClO)_3$, *cis*-$(NSClO)_2(NPCl_2)$, and $(NSClO)(NPCl_2)_2$ †

By **Alan Connelly, Peter Harkins,** and **Andrew L. Porte,*** Department of Chemistry, The University, Glasgow G12 8QQ
Robert A. Shaw, Department of Chemistry, Birkbeck College (University of London), Malet Street, London WC1E 7HX
Johan C. van de Grampel, Department of Inorganic Chemistry, University of Groningen, Nyenborgh 16, 9747 AG, Groningen, The Netherlands

Chlorine-35 n.q.r. spectra for α-$(NSClO)_3$, *cis*-$(NSClO)_2(NPCl_2)$, and $(NSClO)(NPCl_2)_2$ have been recorded in the temperature range 77—300 K. Spectra have also been examined for these substances at 293 K when subjected to pressures within the range 1—700 kg cm^{-2}: the chlorine-35 resonance frequencies are linear functions of pressure. The partial differential coefficients $(\partial\nu/\partial P)_T$ at 293 K, $(\partial\nu/\partial T)_P$ at 1 kg cm^{-2} and 293 K, and $(\partial\nu/\partial T)_V$ at 293 K have been evaluated for each resonance frequency and are related to the molecular conformers present in these solids. At 165 K $(NSClO)(NPCl_2)_2$ undergoes a phase change in which the conformation of the six-membered ring changes. The chlorine resonance frequencies, ν/MHz, are related to the corresponding bond lengths, d/Å: these relationships are $d = -0.0152\nu + 2.4166$ for P–Cl bonds and $d = -0.0172\nu + 2.636$ for S–Cl bonds. The NSClO group is more electronegative than the $NPCl_2$ group. Chlorine valence-electron populations, ϕ, can be deduced from the corresponding chlorine-35 n.q.r. frequencies at 77 K. The appropriate relationships are $\phi = -0.034_5\nu + 8$ for P–Cl bonds and $\phi = -0.026_5\nu + 8$ for SClO groups.

CHLORINE-35 n.q.r. spectroscopy has turned out to be a very useful technique for studying derivatives of hexachlorocyclotriphosphazatriene, $N_3P_3Cl_6$. The chlorine resonance frequencies, and their temperature and pressure coefficients, can be correlated with P–Cl bond lengths and with the valence-shell electronic populations localized on the chlorine atoms. The n.q.r. information can be used to discriminate between positional isomers, between geometrical isomers, and between molecular conformers, and it gives useful information about molecular motions in the solid state.[1]

X-Ray analyses [2-5] and quantum-chemical and basicity investigations [6] have been carried out on the six-membered ring compounds α-$(NSClO)_3$, *cis*-$(NSClO)_2(NPCl_2)$, $(NSClO)(NPCl_2)_2$, and $(NPCl_2)_3$, and their chemistry has been reviewed.[7,8] Whitehead and his co-workers [9-11] have examined the chlorine-35 n.q.r. spectra of the first, second, and fourth members of this sequence within the temperature range 77—300 K, and a detailed analysis of the temperature and pressure dependence of the chlorine-35 resonance frequencies in $N_3P_3Cl_6$ has been made.[1] In this paper we present data obtained from more detailed studies of chlorine-35 n.q.r. in α-$(NSClO)_3$, *cis*-$(NSClO)_2(NPCl_2)$, and $(NSClO)(NPCl_2)_2$ and discuss their significance.

EXPERIMENTAL AND RESULTS

Pressure Effects.—Within the pressure range 1—700 kg cm^{-2}, the resonance frequencies at 293 K were found to be linear functions of the applied pressure; the relationships connecting frequency with pressure are summarized in Table 1.

Temperature Effects.—The chlorine-35 n.q.r. frequencies for α-$(NSClO)_3$ at atmospheric pressure, over the temperature range 77—295 K, are plotted in Figure 1. The resonance frequencies for $(NSClO)_2(NPCl_2)$, over a similar temperature range, have already been examined by Whitehead and his co-workers [11] and our results are very similar except that we detect small cusps in the frequency *vs.* temperature plots for all resonances at *ca.* 190 K. The corresponding variations in the chlorine resonance frequencies in $(NSClO)(NPCl_2)_2$ are shown in Figure 2. At temperatures over 200 K all frequencies can be fitted to polynomials of the form $\nu = a + b'T + (c'/T)$ and least-squares fits of the experimental data to such relationships are listed in Table 2. Resonance frequencies at 77 and 293 K are listed for each compound in Table 3.

TABLE 1

Polynomials for the variation of chlorine-35 n.q.r. frequencies, ν/MHz, with applied pressure, P/kg cm^{-2}, within the range 1—700 kg cm^{-2} at 293 K *

Compound	Polynomial
α-$(NSClO)_3$	$\nu_1{}^2 = 36.130 + (5.69 \times 10^{-5}P)$
	$\nu_2{}^1 = 36.443 + (7.45 \times 10^{-5}P)$
cis-$(NSClO)_2(NPCl_2)$	$\nu_1{}^1 = 28.665 + (3.67 \times 10^{-5}P)$
	$\nu_2{}^1 = 29.834 + (2.99 \times 10^{-5}P)$
	$\nu_3{}^1 = 34.514 + (5.16 \times 10^{-5}P)$
	$\nu_4{}^1 = 35.469 + (5.94 \times 10^{-5}P)$
$(NSClO)(NPCl_2)_2$	$\nu_1{}^1 = 27.862 + (4.719 \times 10^{-5}P)$
	$\nu_2{}^1 = 28.517 + (4.767 \times 10^{-5}P)$
	$\nu_3{}^1 = 28.719 + (5.543 \times 10^{-5}P)$
	$\nu_4{}^1 = 29.121 + (5.471 \times 10^{-5}P)$
	$\nu_5{}^1 = 33.450 + (4.74 \times 10^{-5}P)$

* Superscripts to frequencies represent relative intensities.

Table 4 lists experimental values of $(\partial\nu/\partial P)_T$ at 293 K and

$$\left(\frac{\partial\nu}{\partial T}\right)_V = \left(\frac{\partial\nu}{\partial T}\right)_P + \frac{\alpha}{\beta}\left(\frac{\partial\nu}{\partial P}\right)_T \qquad (i)$$

$(\partial\nu/\partial T)_P$ at 1 kg cm^{-2} and 293 K along with values of $(\partial\nu/\partial T)_V$ at 293 K obtained from the relationship (i), where α is the volume coefficient of thermal expansion and β is

---

† Systematic names for the three compounds are: 1,3,5-trichloro-1,3,5-trioxo-1λ^6,3λ^6,5λ^6,2,4,6-trithiatriazine; 1,3,5,5-tetrachloro-1,3-dioxo-1λ^6,3λ^6,2,4,6,5λ^5-dithiatriazaphosphorine; and 1,3,3,5,5-pentachloro-1-oxo-1λ^6,2,4,6,3λ^5,5λ^5-thiatriazadiphosphorine respectively, where the lamdas indicate the ' abnormal ' connectivities of phosphorus and sulphur.

the compressibility of the solid; the quotient α/β has been taken to be 23 kg cm^{-2} K^{-1}.[12]

DISCUSSION

The effects of temperature changes on n.q.r. frequencies are explained by the Bayer–Kushida theory [13-15] in terms of the vibrational motions in the solid. These cause the effective electric-field gradient and asymmetry parameter for each chlorine nucleus to change with vibration amplitude; larger amplitudes of vibration are more influenced by a given change in temperature, and hence numerically larger temperature coefficients of quadrupole resonance frequencies must be associated with larger amplitudes of nuclear motion.[1]

TABLE 2

Least-squares fits of the form $\nu = a + b'T + (c'/T)$ to the experimental curves of n.q.r. frequency *vs.* temperature [a]

Compound	Resonance [b]	$10^{-6}a$/ Hz	b'/ Hz K^{-1}	$10^{-6}c'$/ Hz K
α-(NSClO)$_3$	$\nu_1{}^2$	38.554	−6 564	−146.69
	$\nu_2{}^1$	38.269	−5 295	−80.58
cis-(NSClO)$_2$(NPCl$_2$)	$\nu_1{}^1$	29.285	−2 437	27.548
	$\nu_2{}^1$	30.606	−2 786	12.870
	$\nu_3{}^1$	35.562	−3 445	−11.243
	$\nu_4{}^1$	36.799	−4 339	−17.151
(NSClO)(NPCl$_2$)$_2$	$\nu_1{}^1$	33.127	−13 135	−415.01
	$\nu_2{}^1$	34.534	−14 850	−488.06
	$\nu_3{}^1$	32.968	−10 593	−335.67
	$\nu_4{}^1$	33.356	−10 442	−344.42
	$\nu_5{}^1$	40.291	−16 320	−603.3

[a] These data are valid for temperatures above 200 K.
[b] Superscripts to frequencies represent relative intensities.

Application of pressure can be considered to have two main effects on n.q.r. data. Isotropic compression of solids reduces the amplitudes of nuclear motions and hence increases n.q.r. frequencies; this is the so-called ‘ dynamic ’ influence of isotropic compression and it makes positive contributions to the pressure coefficients $(\partial\nu/\partial P)_T$. In anisotropic solids, hydrostatic compression causes shearing movements to take place and alters relative co-ordinates of molecules. The magnitudes and signs of the contributions made by such ‘ static ’ distortions to electric-field gradients and to $(\partial\nu/\delta P)_T$ depend on the crystal and molecular geometries and on the crystal and molecular polarizabilities, and so their contributions to $(\partial\nu/\partial P)_T$ may either reinforce or oppose the contributions from ‘ dynamic ’ effects. Motional amplitudes of nuclei in overcrowded sites in molecules are relatively restricted, so both dynamic and static effects make smaller contributions to $(\partial\nu/\partial P)_T$ in overcrowded sites; if the static contribution predominates then negative values of $(\partial\nu/\partial P)_T$ may be obtained.[1]

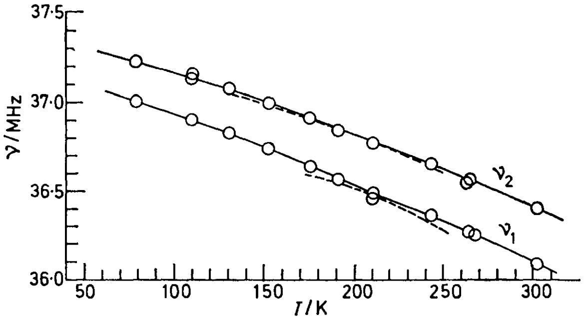


FIGURE 1 Chlorine-35 n.q.r. frequencies *vs.* temperature for α-(NSClO)$_3$

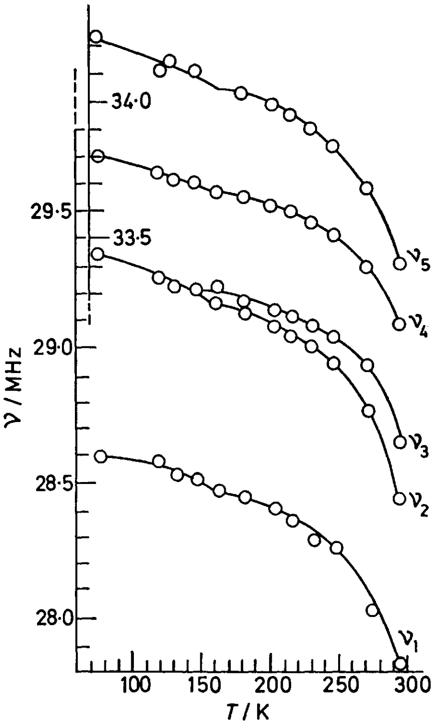


FIGURE 2 Plot of chlorine-35 n.q.r. frequencies *vs.* temperature for (NSClO)(NPCl$_2$)$_2$. Upper scale applies to ν_5 values only

α-(NSClO)$_3$.—The n.q.r. data in Tables 1—4 show that two of the chlorine atoms in this molecule are equivalent. Isotropic motion of a rigid planar N$_3$S$_3$ ring would require all $\partial\nu/\partial T$ values in the molecule to be almost identical. The data in Table 4 therefore show that the N$_3$S$_3$ ring cannot be planar and examination of molecular models shows that the results are not consistent with a 1-*cis*-3-*cis*-5-*trans* structure but they are consistent with the all-*cis* slight chair structure, (1), derived by the *X*-ray crystallographers; [2] it is important to note that in all

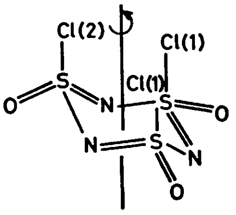
TABLE 3

Chlorine-35 n.q.r. frequencies

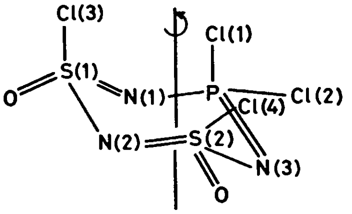
Compound	Resonance *	Frequency/MHz At 77 K	Frequency/MHz At 293K
α-(NSClO)$_3$	$\nu_1{}^2$	37.000	36.130
	$\nu_2{}^1$	37.225	36.443
cis-(NSClO)$_2$(NPCl$_2$)	$\nu_1{}^1$	29.330	28.665
	$\nu_2{}^1$	30.481	29.834
	$\nu_3{}^1$	35.205	34.514
	$\nu_4{}^1$	36.331	35.469
(NSClO)(NPCl$_2$)$_2$	$\nu_1{}^1$	28.595	27.862
	$\nu_2{}^1$	29.345	28.517
	$\nu_3{}^1$		28.719
	$\nu_4{}^1$	29.702	29.121
	$\nu_5{}^1$	34.245	33.450

* Superscripts to frequencies represent relative intensities.

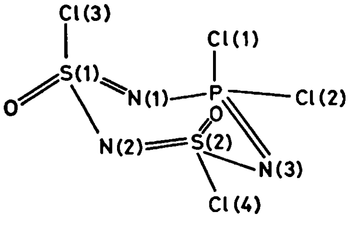
the structures shown here the distortions from planarity are greatly exaggerated for illustrative purposes. The n.q.r. data show that the mirror plane is preserved over the temperature range 77—300 K, and also when the solid is subjected, at 300 K, to hydrostatic pressure. All the chlorine atoms are axial, and Table 4 enables the quadrupole resonance signals to be assigned to the correspondingly numbered chlorine nuclei in (1). To account for the data in Table 4 libration about the axis shown in (1) must be slightly preferred; Cl(2) has a slightly smaller amplitude of vibration and therefore $|\partial\nu_1/\partial T|$ is larger than $|\partial\nu_2/\partial T|$. Furthermore, since the Cl(1) atoms are now more overcrowded than Cl(2), $\partial\nu_1/\partial P$ is smaller than $\partial\nu_2/\partial P$.



(1)



(2a)



(2b)

cis-$(NSClO)_2(NPCl_2)$.—The two largest frequencies detected in this compound can be assigned to the *S*-bonded chlorine atoms but the n.q.r. results by themselves are unable to distinguish between the structures (2a) and (2b). In the distorted slight chair *cis* structure, (2a), S(2) lies only very slightly above the plane formed by N(1), P, and N(2). S(1) moves up out of the plane and N(3) down. The very similar *trans* structure (2b) is also consistent with the n.q.r. results but *X*-ray analysis shows that in fact (2a) essentially correctly describes the conformation of this molecule.[3]

$(NSClO)(NPCl_2)_2$.—Figure 2 shows that for this compound a structural change takes place when the temperature is raised above *ca.* 165 K and, furthermore, this change must be such that the effective equivalence in the electric-field gradients at Cl(2) and Cl(3) in the low-temperature form is absent in the high-temperature form of this compound. The *X*-ray analysis of this solid, carried out by van Bolhuis and van de Grampel,[4]

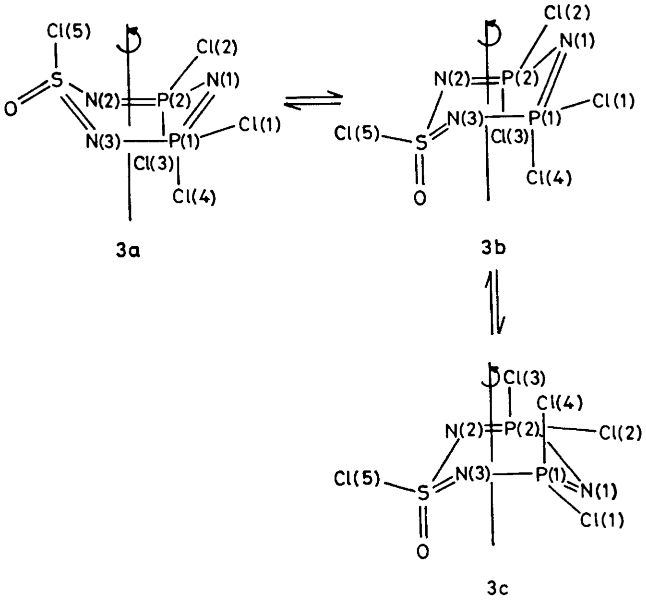


TABLE 4

Differential coefficients for α-$(NSClO)_3$, *cis*-$(NSClO)_2(NPCl_2)$, and $(NSClO)(NPCl_2)_2$ [a]

Compound	Resonance [b]	$(\partial\nu/\partial P)_T$ at 293 K	$(\partial\nu/\partial T)_P$ at 1 kg cm^{-2} and 293 K	$(\partial\nu/\partial T)_V$ at 293 K
α-$(NSClO)_3$	ν_1^2	56.9	−4 855	−3 546
	ν_2^1	74.5	−4 357	−2 644
cis-$(NSClO)_2(NPCl_2)$	ν_1^1	36.7	−2 758	−1 914
	ν_2^1	29.9	−2 936	−2 248
	ν_3^1	51.6	−3 314	−2 127
	ν_4^1	59.4	−4 139	−2 773
$(NSClO)(NPCl_2)_2$	ν_1^1	47.2	−8 301	−7 215
	ν_2^1	47.7	−9 165	−8 068
	ν_3^1	55.4	−6 683	−5 409
	ν_4^1	54.7	−6 430	−5 172
	ν_5^1	47.4	−9 293	−8 203

[a] $(\partial\nu/\partial P)_T$ values are in units of Hz cm^2 kg^{-1}. Values of $(\partial\nu/\partial T)_P$ and of $(\partial\nu/\partial T)_V$ are in units of Hz K^{-1}. [b] Superscripts to frequencies represent relative intensities.

shows that, at 133 K, the ring has a slight boat conformation, (3a), and this analysis enables us to assign chlorine n.q.r. signals to the correspondingly numbered atoms: the *X*-ray and n.q.r. results, taken in conjunction, show that the bond lengths decrease in the sequence P(1)–Cl(1) > P(2)–Cl(2) ≈ P(2)–Cl(3) > P(1)–Cl(4).

The n.q.r. data in Figure 2 and in Table 4 show that at 293 K the amplitudes of librational motions in (NSClO)-$(NPCl_2)_2$ are considerably greater than the corresponding motions in α-$(NSClO)_3$, *cis*-$(NSClO)_2(NPCl_2)$, and in $(NPCl_2)_3$. The data also show that the N_3P_2S ring in this molecule cannot be planar and, moreover, the 293 K data are not consistent with the slight boat, low-temperature form. In particular, the large $|\partial\nu_5/\partial T|$ values show that in the high-temperature form Cl(5) must be pseudo-equatorial and the pattern of three large and two small $|\partial\nu/\partial T|$ values, the pattern of $\partial\nu/\partial P$ values, the inequivalence of Cl(2) and Cl(3), and the sequence of resonance frequencies for Cl(1), Cl(2), Cl(3), and Cl(4) are all consistent with either a conformation approximating to the slight chair form [exaggerated in (3b)] or to a conformation approximating to the slight boat form [exaggerated in (3c)], in which rigid librational motions about the axes shown are preferred, and where the chlorine atoms are assigned to the correspondingly numbered frequencies in Table 4: an *X*-ray analysis of the high-temperature form is needed to unambiguously determine its structure. The interconversions (ii) only require relatively small movements of the atoms. The energies of these three conformations must be very similar and the molecular shapes and electron distributions in the three conformations are much the same, so it

$$\text{(3a)(slight boat form)} \rightleftharpoons \text{(3b)(slight chair form)} \rightleftharpoons \text{(3c)(slight boat form)} \qquad \text{(ii)}$$

is not too surprising that neither a Guinier powder diagram from 248 to 133 K nor a differential thermal analysis in the range 126—273 K give any indication for this phase transition.

TABLE 5

Observed and predicted P–Cl bond lengths, *d*/Å, and corresponding chlorine-35 n.q.r. frequencies, ν/MHz, at 77 K

				d/Å	
Compound	Ref.	Resonance	ν/MHz at 77 K	Expt.	Predicted from (iii)
$N_3P_3Cl_6$	1, *a*	ν_1^2	28.318	1.988(3)	1.986
		ν_2^1	28.328	1.986(3)	1.986
		ν_3^1	28.598	1.984(2)	1.982
		ν_4^2	28.684	1.984(2)	1.981
$N_3P_3Ph_2Cl_4$	1, *b*	ν_1^1	27.091	2.010(2)	2.005
		ν_2^1	27.619	2.002(2)	1.997
		ν_3^1	28.079	1.990(2)	1.990
		ν_4^1	28.248	1.989(2)	1.987
$N_3P_3Ph_4Cl_2$	1, *c*	ν_1^1	26.341	2.024(5) 2.030(5)	2.016
		ν_2^2	26.436	2.008(5)	2.015
		ν_3^3	26.755	2.005(5)	2.010
gem-$N_3P_3Cl_3(NMe_2)_3$	1, *d*	ν_1^2	23.974	2.049(2)	2.052
		ν_2^1	26.84	2.010(2)	2.009
		ν_3^4	27.574	1.992(2)	1.997
cis-$N_3P_3Cl_4(NMe_2)_2$	16	ν_1^2	24.054	2.052(2)	2.051
		ν_2^1	27.375	1.991(3)	2.000
		ν_3^1	28.090	1.986(3)	1.990
trans-$N_3P_3Cl_4(NMe_2)_2$	16	ν_1^1	24.172	2.036(3)	2.049
		ν_2^1	24.670	2.027(3)	2.042
		ν_3^1	27.680	1.985(3)	1.996
		ν_4^1	27.569	1.990(3)	1.998
cis-$(NSClO)_2(NPCl_2)$	3	ν_1^1	29.330	1.960(6)	1.971
		ν_2^1	30.481	1.954(6)	1.953
$(NSClO)(NPCl_2)_2$ [e]	4	ν_1^1	28.595	1.982(1)	1.982
		ν_2^1 ν_3^1	29.345	1.979(1) 1.975(1)	1.971
		ν_4^1	29.702	1.969(1)	1.965

[a] G. J. Bullen, *J. Chem. Soc.* (*A*), 1971, 1450. [b] N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, 1965, **19**, 693. [c] N. V. Mani, F. R. Ahmed, and W. H. Barnes, *Acta Cryst.*, 1966, **21**, 375. [d] F. R. Ahmed and D. R. Pollard, *Acta Cryst.*, 1972, **B28**, 513. [e] These assignments are only valid for structures (3a) and (3b).

P–Cl *Bond Lengths*.—Phosphorus–chlorine bond lengths in *cis*-$(NSClO)_2(NPCl_2)$ and in $(NSClO)(NPCl_2)_2$ are shorter than the P–Cl bond lengths in the derivatives of hexachlorocyclotriphosphazatriene, and the related chlorine-35 n.q.r. frequencies are correspondingly higher. These two compounds therefore enable us to further test the relationship $d = -0.012_8\nu + 2.355$ between P–Cl bond lengths, *d*/Å, and corresponding chlorine-35 n.q.r. frequencies at 77 K, ν/MHz, derived from earlier studies carried out on the chlorocyclotriphosphazatrienes.[1] These additional data, plus data supplied by Dr. F. R. Ahmed [16] for *cis*- and *trans*-$N_3P_3Cl_4(NMe_2)_2$, indicate that the relationship should be slightly modified to (iii).

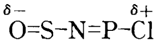
$$d = -0.015\,2\nu + 2.416\,6 \qquad \text{(iii)}$$

The experimental bond lengths for 28 P–Cl bonds encountered in eight compounds are compared in Table 5 with the P–Cl bond lengths predicted from equation (iii). The *X*-ray and n.q.r. results and quantum-chemical calculations[6] consistently show that NSClO is a more electronegative residue than $NPCl_2$, so that each time a PCl_2 group in the $N_3P_3Cl_6$ structure is replaced by an SClO residue electrons are pulled away from the remaining PCl_2 groups, thereby making the P–Cl residues less ionic and shortening the P–Cl bond lengths. Furthermore, the *X*-ray and n.q.r. results show that, although the differences are hardly significant when considering a compound in isolation, the P–Cl bonds *cis* to S=O are shorter than the P–Cl bonds *trans* to S=O; P–Cl bonds *cis* to S=O are therefore rather less ionic than P–Cl bonds *trans* to S=O. A '*cis* effect' has previously been invoked[17] in order to account for n.m.r. data and for some of the reactions encountered in substituted cyclotriphosphazatrienes. In it, electrons appear to be more readily transferred between two groups situated on neighbouring phosphorus atoms which are *cis* to one another, than between two such groups *trans* to one another. Another *cis* effect, shown in (4), may operate in the mixed-ring systems described in this paper.

TABLE 6

Observed and predicted S–Cl bond lengths, d/Å, and corresponding chlorine-35 n.q.r. frequencies, ν/MHz, at 77 K

Compound	Ref.	Bond	ν/MHz at 77 K	d/Å Expt.	d/Å Predicted from (iv)
α-$(NSClO)_3$	3	S–Cl(1)	37.000	1.999(4)	2.000(5)
		S–Cl(2)	37.225	2.007(4)	1.996(5)
cis-$(NSClO)_2(NPCl_2)$	3	S–Cl(3)	35.205	2.028(6)	2.031(5)
		S–Cl(4)	36.331	2.007(6)	2.011(5)
$(NSClO)(NPCl_2)_2$	4	S–Cl(5)	34.245	2.048(1)	2.047(5)



$$\overset{\delta-}{O}{=}S{-}N{=}P{-}\overset{\delta+}{Cl}$$

(4)

S–Cl *Bond Lengths*.—Sulphur–chlorine bond lengths, d/Å, in α-$(NSClO)_3$, *cis*-$(NSClO)_2(NPCl_2)$, and $(NSClO)(NPCl_2)_2$, and the corresponding chlorine-35 n.q.r. frequencies, ν/MHz, are found to be linearly connected by the relationship (iv). Observed and predicted S–Cl

$$d = -0.017\,2\nu + 2.636 \tag{iv}$$

bond lengths are compared in Table 6. The comparison confirms that NSClO is more electronegative than $NPCl_2$ and that electrons are released into neighbouring NSClO residues when $NPCl_2$ replaces an NSClO group. Replacement by $NPCl_2$ makes the neighbouring S–Cl bonds more ionic, the S–Cl bond lengths increase, and the corresponding chlorine-35 n.q.r. frequencies decrease.

Chlorine Electron Populations.—We have not measured asymmetry parameters in any of these compounds but Lucken[18] has shown that chlorine asymmetry parameters lie within the range 0—0.02 in $N_3P_3Cl_6$, and if these small values are also appropriate to α-$(NSClO)_3$, *cis*-$(NSClO)_2(NPCl_2)$, and $(NSClO)(NPCl_2)_2$ then π character cannot contribute any more than *ca.* 0.3% to the nature of the bonds to the chlorine atoms in these molecules. CNDO/2 quantum-chemical calculations of ϕ_{Cl}, the valence-shell electronic populations that can be statistically considered to be localized on the chlorine atoms, have been carried out for these compounds[6] and comparison of the calculated ϕ values with the corresponding chlorine-35 n.q.r. frequencies shows that the two are linearly connected by the relationship (v) for P–Cl bonds and (vi) for OS–Cl bonds. In these expressions ν/MHz

$$\phi_{\mathrm{Cl}} = -0.034_5\nu + 8 \tag{v}$$

$$\phi_{\mathrm{Cl}} = -0.026_5\nu + 8 \tag{vi}$$

is the resonance frequency recorded at 77 K. When allowance is made for differential contributions due to crystal-structure effects it now follows that chlorine-35 n.q.r. frequencies enable estimates of the relative chlorine electron populations in these molecules to be made with precisions of $\pm 0.015e$, and so can be used to quantitatively estimate relative electron affinities of neighbouring substituents.

We wish to thank the S.R.C. for providing the Decca n.q.r. equipment used in this work, and Dr. F. R. Ahmed for communicating his results on *cis*- and *trans*-$N_3P_3Cl_4(NMe_2)_2$ prior to publication.

[9/1225 *Received, 3rd August*, 1979]

REFERENCES

[1] A. Connelly, W. H. Dalgleish, P. Harkins, R. Keat, A. L. Porte, I. Raitt, and R. A. Shaw, *J. Magnetic Resonance*, 1978, **30**, 439 and refs. therein.

[2] A. C. Hazell, G. A. Wiegers, and A. Vos, *Acta Cryst.*, 1966, **20**, 186.

[3] J. C. van de Grampel and A. Vos, *Acta Cryst.*, 1969, **B25**, 651.

[4] F. van Bolhuis and J. C. van de Grampel, *Acta Cryst.*, 1976, **B32**, 1192.

[5] G. J. Bullen, *J. Chem. Soc.* (*A*), 1971, 1450.

[6] J. P. Faucher, J. C. van de Grampel, J-F. Labarre, S. N. Nabi, B. De Ruiter, and R. A. Shaw, *J. Chem. Research* (*S*), 1977, 112; (*M*), 1977, 1257, and refs. therein.

[7] R. A. Shaw and M. Woods, *Actes Congr. Int. Composes Phosphores*, 1*st.*, 1977, Inst. Mond Phosphate, Paris, 1978, pp. 249—268.

[8] J. C. van de Grampel, *Actes Congr. Int. Composes Phosphores*, 1*st.*, 1977, Inst. Mond Phosphate, Paris, 1978, pp. 261—276.

[9] M. Kaplansky and M. A. Whitehead, *Canad. J. Chem.*, 1967, **45**, 1669.

[10] M. Kaplansky, R. Clipsham, and M. A. Whitehead, *J. Chem. Soc.* (*A*), 1969, 584.

[11] R. Clipsham, R. M. Hart, and M. A. Whitehead, *Inorg. Chem.*, 1969, **8**, 2431.

[12] W. H. Dalgleish and A. L. Porte, *J. Magnetic Resonance*, 1975, **20**, 359.

[13] H. Bayer, *Z. Phys.*, 1951, **130**, 227.

[14] T. Kushida, *J. Sci. Hiroshima Univ.*, 1955, **A19**, 327.

[15] T. Kushida, G. B. Benedek, and N. Bloembergen, *Phys. Rev.*, 1956, **104**, 1364.

[16] F. R. Ahmed and S. Fortier, *Acta Cryst.*, 1980, in the press.

[17] R. Keat and R. A. Shaw, *J. Chem. Soc.* (*A*), 1966, 908.

[18] E. A. C. Lucken, *Proc. XIth Colloque Ampère*, North Holland, Amsterdam, 1963, p. 678.