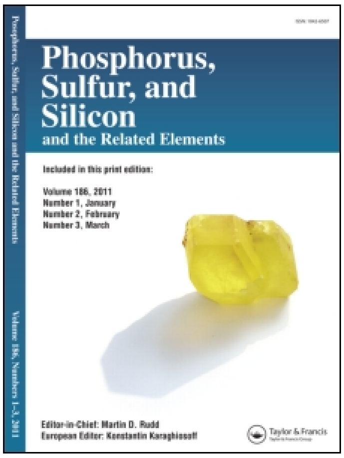


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHETIC NMR SPECTROSCOPIC AND X-RAY CRYSTALLOGRAPHIC STUDIES ON PHOSPHAZENYLCYCLOPHOSPHAZENES

John K. Fincham[a]; Michael B. Hursthouse[b]; Rodney Keat[c]; Harold G. Parkes[a]; David S. Rycroft[c]; Leyl S. Shaw (Née Gözen)[ab]; Robert A. Shaw[a]
[a] Department of Chemistry, Birkbeck College, (University of London), London, U.K. [b] Department of Chemistry, Queen Mary College, (University of London), London, U.K. [c] Department of Chemistry, University of Glasgow, Glasgow, U.K.

To cite this Article Fincham, John K. , Hursthouse, Michael B. , Keat, Rodney , Parkes, Harold G. , Rycroft, David S. , Shaw (Née Gözen), Leyl S. and Shaw, Robert A.(1986) 'SYNTHETIC NMR SPECTROSCOPIC AND X-RAY CRYSTALLOGRAPHIC STUDIES ON PHOSPHAZENYLCYCLOPHOSPHAZENES', Phosphorus, Sulfur, and Silicon and the Related Elements, 28: 1, 175 — 183

To link to this Article: DOI: 10.1080/03086648608072807

URL: http://dx.doi.org/10.1080/03086648608072807

Phosphorus and Sulfur, 1986, Vol. 28, pp. 175–183
0308-664X/86/2802-0175/$15.00/0

SYNTHETIC NMR SPECTROSCOPIC AND X-RAY CRYSTALLOGRAPHIC STUDIES ON PHOSPHAZENYLCYCLOPHOSPHAZENES

JOHN K. FINCHAM,[a] MICHAEL B. HURSTHOUSE,[b]
RODNEY KEAT,[c] HAROLD G. PARKES,[a] DAVID S. RYCROFT,[c]
LEYLÂ S. SHAW (NÉE GÖZEN)[a,b] and ROBERT A. SHAW[a]*

[a]*Department of Chemistry, Birkbeck College, (University of London), Malet Street, London WC1E 7HX, U.K.*
[b]*Department of Chemistry, Queen Mary College, (University of London), Mile End Road, London E1 4NS, U.K.*
[c]*Department of Chemistry, University of Glasgow, Glasgow, G12 8QQ, U.K.*

Some reactions of phosphazenylcyclophosphazenes are reported. Their NMR spectra are discussed and related to conformation. X-ray crystallographic data are presented.

Phosphazenylcyclophosphazenes have attracted a lot of attention in recent times. (e.g. Ref.[1]). Basicity studies[2] and ^{31}P NMR spectroscopy, in particular $^{4}J(P,P)$ values,[3-5] have proved most useful in predicting conformational differences, which were borne out by X-ray crystallographic studies.[6-14]

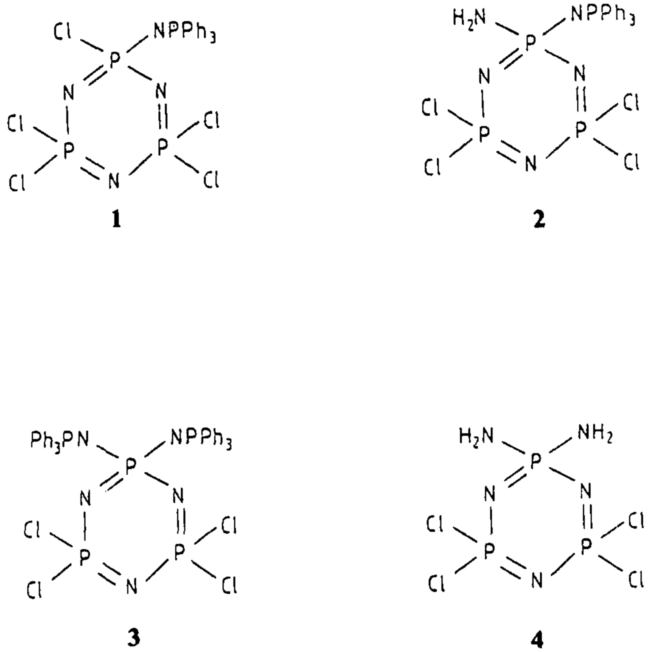
We have concentrated our studies on three compounds (Figure 1), which were prepared by literature methods.[15]

Our studies entailed synthetic, NMR spectroscopic and X-ray crystallographic investigations. We have shown elsewhere[16,17] that geminal $N_3P_3(NH_2)_2Cl_4$, (**4**) forms rearranged, as well as unrearranged products when treated with sodium alkoxide. An extension of this work to geminal $N_3P_3(NPPh_3)(NH_2)Cl_4$, (**2**), showed only unrearranged alcoholysis products, i.e. geminal $N_3P_3(NPPh_3)(NH_2)(OR)_4$. The reaction was slower than with the diamide, (**4**). The replacement of both NH_2 groups in (**4**) by $NPPh_3$ groups to give compound (**3**) made the latter very unreactive, demonstrating that the replacement of an NH_2 group by an $NPPh_3$ group deactivates adjacent PCl_2 groups towards S_{N^2} type nucleophilic attack (Figure 2). This is in contrast to the situation where structural units such as $P(NPPh_3)Cl$ are present, when an S_{N^1} type nucleophilic attack is favoured.[5]

A detailed NMR spectroscopic study of compounds (**1**), (**2**) and (**3**) was carried out simultaneously with the structural investigation of compound (**2**) by X-ray crystallography, and the reinvestigation of compound (**1**)[18] to obtain more accurate parameters than were obtained from the earlier photographic investigation.[7,9] We have defined conformational Types I, II and III elsewhere.[19-21] We have also defined Types I and II more precisely in crystallographic terms.[4] We now extend this to Type III (Figure 3).

---

*Author to whom all correspondence should be addressed.



1 **2** **3** **4**

FIGURE 1 Display diagrams of compounds (1–4).

$$N_3P_3(NH_2)_2Cl_4 + NaOR \longrightarrow N_3P_3(NH_2)_2(OR)_4$$

rearranged and unrearranged

$$N_3P_3(NPPh_3)(NH_2)Cl_4 + NaOR \longrightarrow N_3P_3(NPPh_3)(NH_2)(OR)_4$$

unrearranged

$$N_3P_3(NPPh_3)_2Cl_4 + NaOR \longrightarrow \text{no reaction}$$

FIGURE 2 Reactions of $N_3P_3XYCl_4$ ($X = Y = NH_2$, $NPPh_3$; $X = NH_2$, $Y = NPPh_3$) with NaOR.

Compound (**1**) represents an example of Type I conformation,[7,9,18] compound (**3**)[12] and geminal $N_3P_3(NPPh_3)PhCl_4$[6] represent Type II behaviour. Previously, no pure Type III conformation has been observed crystallographically for phosphazenylcyclophosphazenes, although geminal $N_3P_3(NPPh_3)(NEt_2)Cl_4$ showed a behaviour intermediate between Types II and III with a dihedral angle of 154°.[11]

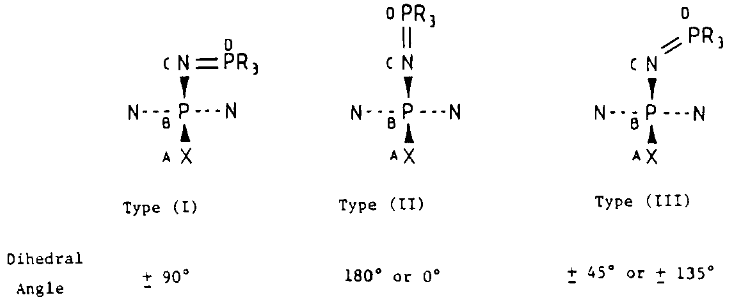


FIGURE 3 Conformational Types I, II and III together with their dihedral angles.

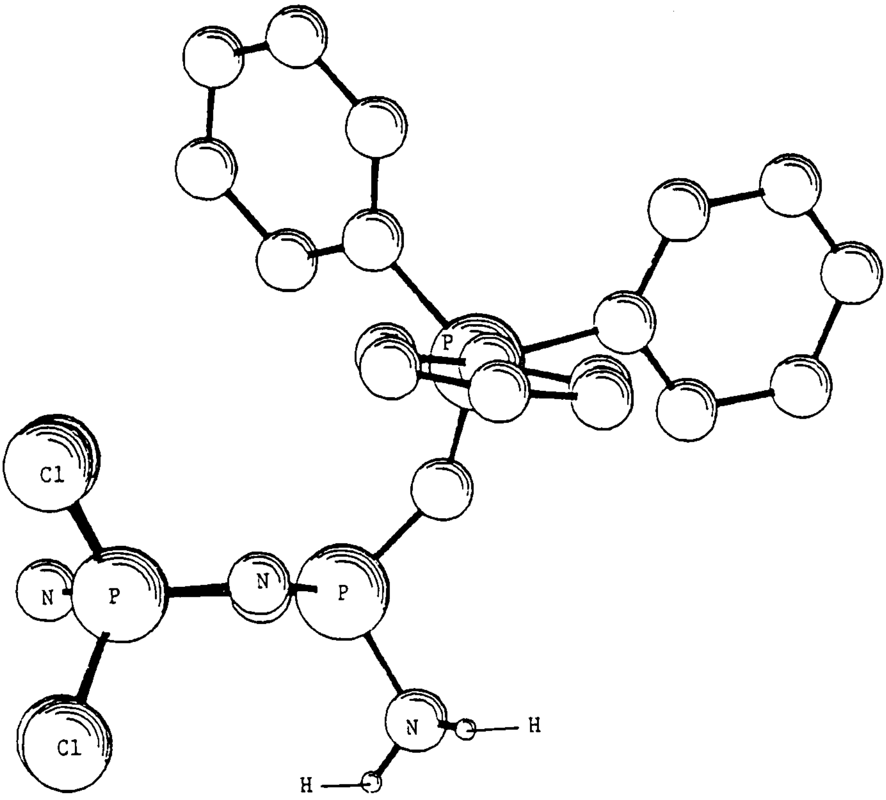


FIGURE 4 Molecular diagram of $N_3P_3(NPPh_3)(NH_2)Cl_4$.

We now report the first example of an almost pure Type III conformation. Geminal $N_3P_3(NPPh_3)(NH_2)Cl_4$(**2**) has a dihedral angle of 139.2°. Its structure is shown in Figure 4.

Compound (**2**) represents the first phosphazenylcyclophosphazene capable of hydrogen bonding that has been crystallographically investigated. Compound (**2**) forms hydrogen-bonded dimers (Figure 5).

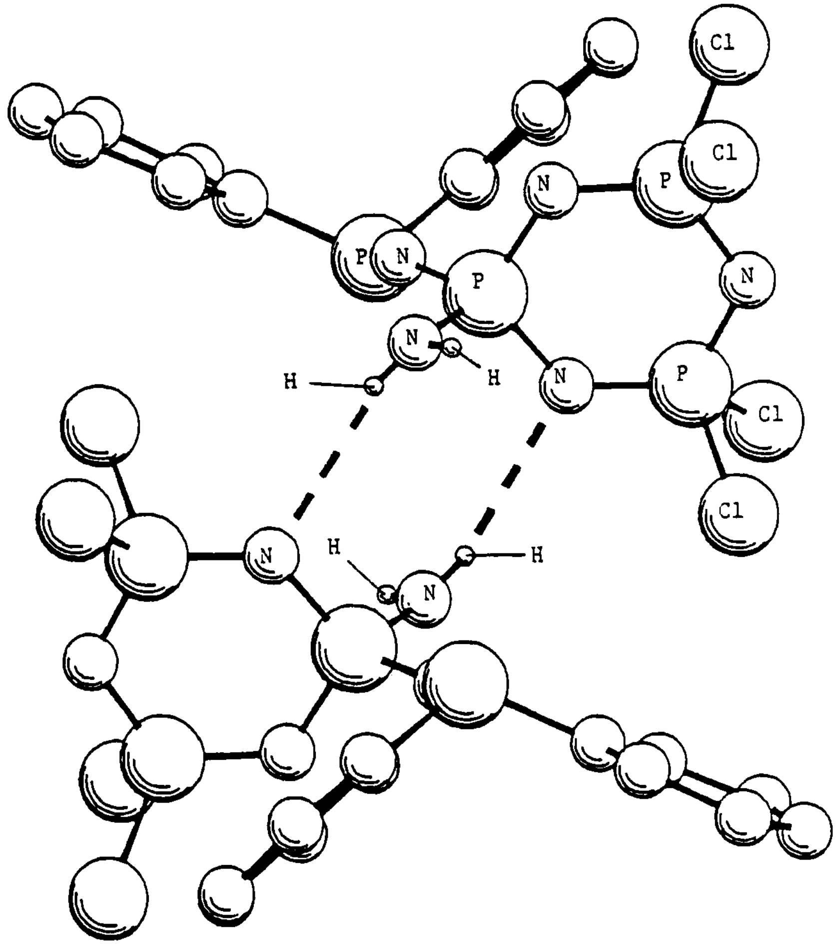


FIGURE 5 Hydrogen bonded dimer of $N_3P_3(NPPh_3)(NH_2)Cl_4$. For the sake of clarity one Ph group is omitted from each molecule.

One N—H bond from the NH_2 group bonds to the ring nitrogen atom *ortho* to the phosphorus carrying the two nitrogenous substituents resulting in an eight-membered hydrogen-bonded ring. This dimeric hydrogen-bonded structure closely resembles that of geminal $N_3P_3(NHBu^t)_2Cl_4$.[22]

A closer inspection of the conformational types mentioned above requires a further refinement in that *syn* and *anti* conformations must be considered. Orthographic projections[4,23] make this particularly clear (Figure 6).

Thus with compound (**1**) having Type I conformation, we can consider a "frozen" situation where one PCl_2 group is *syn*, the other PCl_2 group *anti*, to the $NPPh_3$ substituent. In compound (**3**) we can similarly see that in a Type II situation, one $NPPh_3$ group is *syn*, the other $NPPh_3$ group is *anti*, with respect to the N_3P_3 ring.

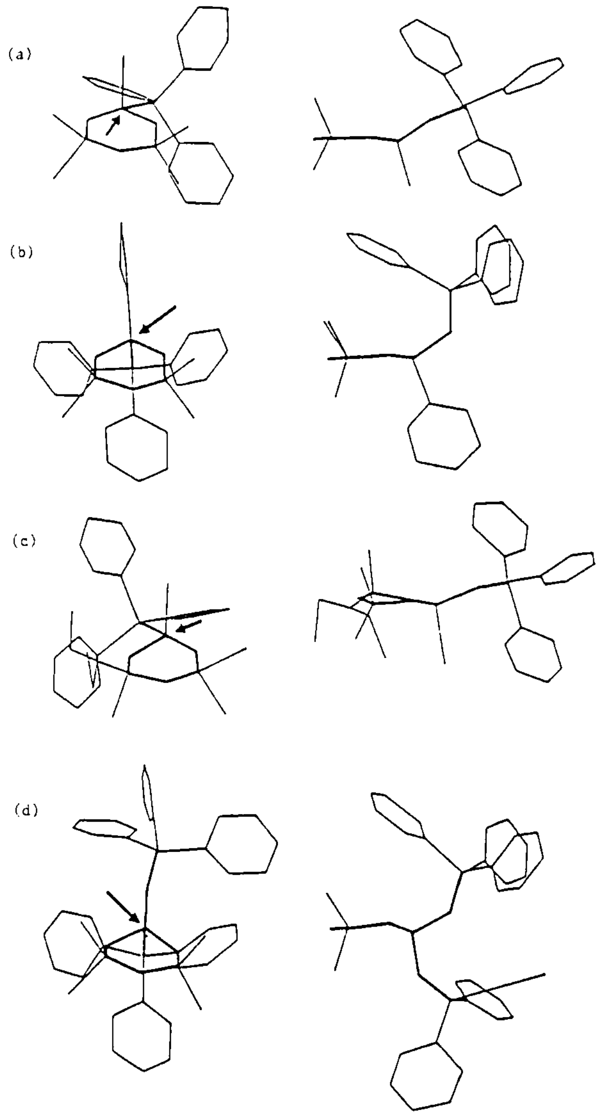


FIGURE 6 Solid state conformational features of selected phosphazenyl derivatives. Bolder lines show the P—N skeletal detail, except that for the P—NEt_2. The left-hand column shows a projection along the first *exo* P—N bond (arrowed), and the right-hand column shows a projection across the cyclophosphazene ring perpendicular to the same P—N bond. (a) $N_3P_3Cl_5(N{=}PPh_3)$.[10] (b) $N_3P_3Cl_4Ph(N{=}PPh_3)$ (geminal).[6] (c) $N_3P_3(NEt_2)(N{=}PPh_3)$ (nongeminal).[14] (d) $N_3P_3(N{=}PPh_3)_2$ (geminal)[12]

We have attempted to "freeze" out such conformations, i.e. to make rotation around the exocyclic P—N bond of the $NPPh_3$ substituent slow on the NMR time scale. We studied the ^{31}P NMR spectra of compounds (**1**) and (**3**) in acetone over the temperature range, room temperature down to −85°C.

In Figure 7 we show the spectrum of compound (**1**), (a) at room temperature and (b) at −85°C, both at 24.15 MHz. Additional lines appeared at low temperature,

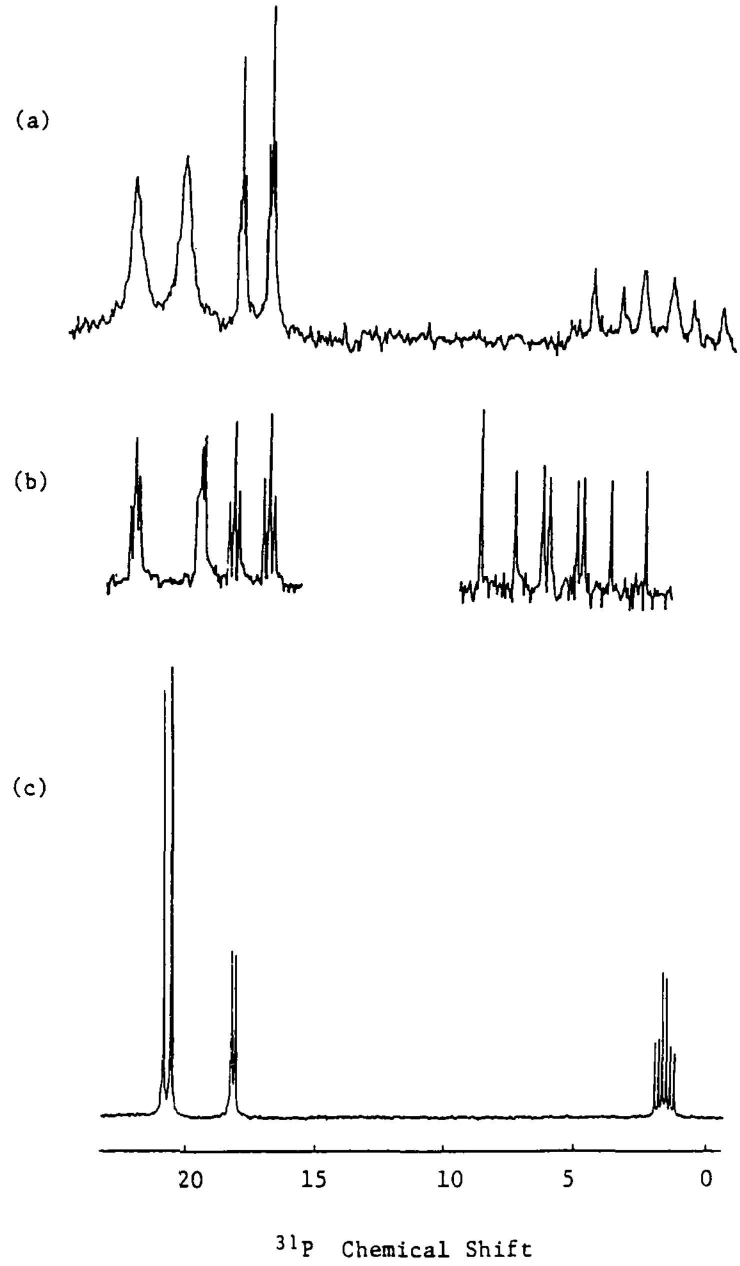


FIGURE 7 $^{31}P\{H\}$ NMR spectra of $N_3P_3Cl_5(NPPh_3)$ (1) in acetone (a) at room temperature (24.15 MHz), (b) at −85°C (24.15 MHz), and (c) at −85°C (162 MHz).

which however were not observed at low temperature at higher field. The high field spectrum (162.0 MHz) at −85°C is shown in Figure 7c.

If we simulate the ^{31}P NMR spectrum of compound (1) using the parameters determined from the spectrum at 24.15 MHz (−85°C) i.e. δ $\underline{P}Cl_2 = 20.3$, δ $\underline{P}(Cl)N{=}PPh_3$ = 0.2, δ $\underline{P}Ph_3$ = 15.4 ppm, $^2J(P,P)$ *endo* 47.9, *exo* 25.1 and $^4J(P,P)$ 3.5 Hz we find a very good fit (Figure 8). Upon simulation of the spectrum at 162 MHz using these parameters we find that some of the fine structure due to the four-bond coupling has remained, but that the remaining fine structure observed at 24.15 MHz (at −85°C) has disappeared and is therefore due to second-order effects. We can therefore deduce that freezing out of rotational conformers has not occurred in these experiments.

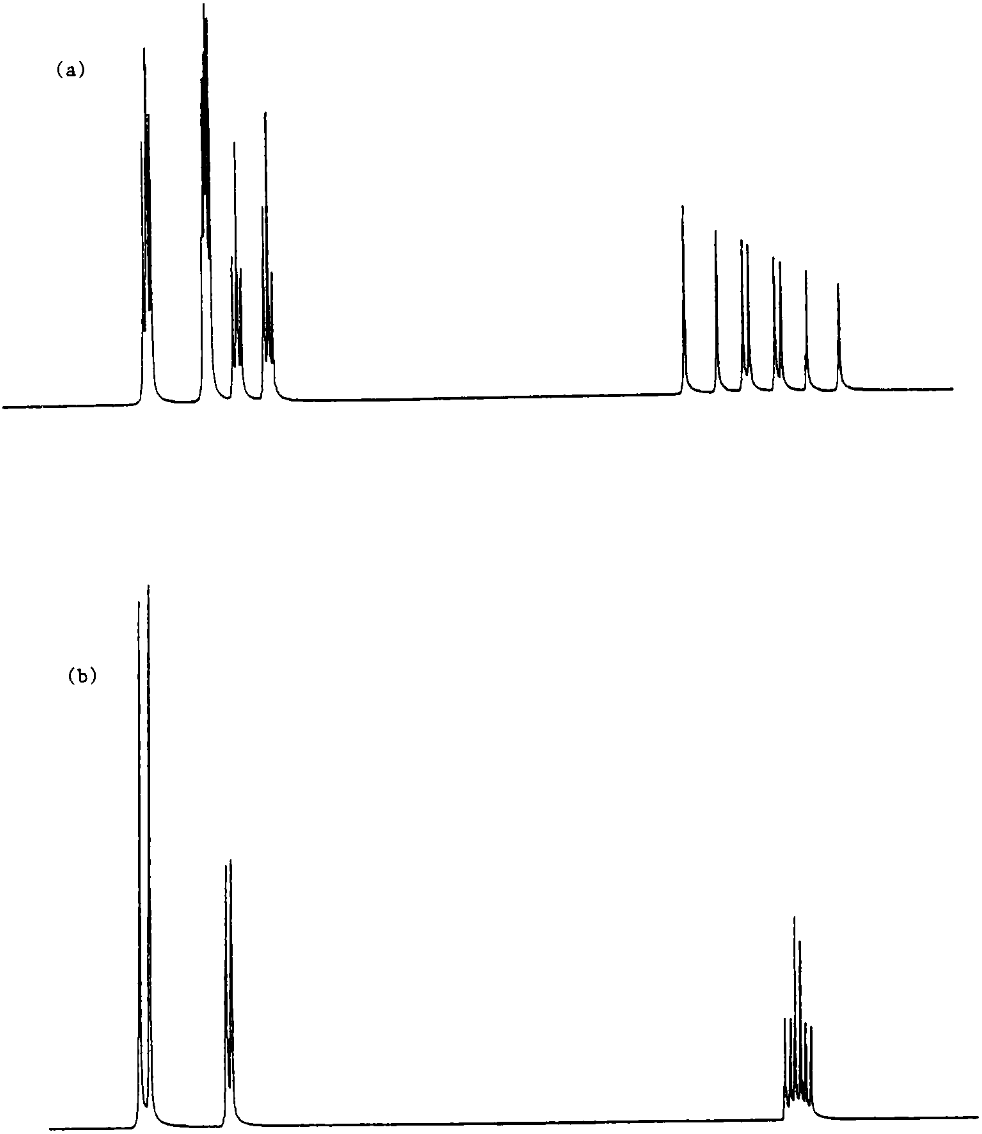


FIGURE 8 Spin simulation of the $^{31}P\{H\}$ NMR spectra of $N_3P_3Cl_5(NPPh_3)$ (**1**) from the data obtained from the spectrum shown in Figure 7(b) i.e. δ $\underline{P}Cl_2$ = 20.3, δ $\underline{P}(Cl)N{=}PPh_3$ = 0.2, δ $\underline{P}Ph_3$ = 15.4, $^2J(P,P)$ *endo* = 47.9, *exo* = 25.1 and $^4J(P,P)$ = 3.5 Hz (a) 24 MHz and (b) 162 MHz.

We have thus demonstrated that temperatures of −85°C in acetone are not sufficiently low to show hindered rotation in these compounds, either in Type I or Type II conformation. We are pursuing our studies at even lower temperatures.

We have shown elsewhere[3,4,23] that compounds with Type I conformation show $^4J(\mathrm{P,P})$ coupling constants in the range of 3.3 to 5.7 Hz, whilst those compounds with Type II conformation or approximating to it, have $^4J(\mathrm{P,P})$ values close to zero. As compound (**2**), $N_3P_3(NPPh_3)(NH_2)Cl_4$, shows no four-bond coupling, we believe

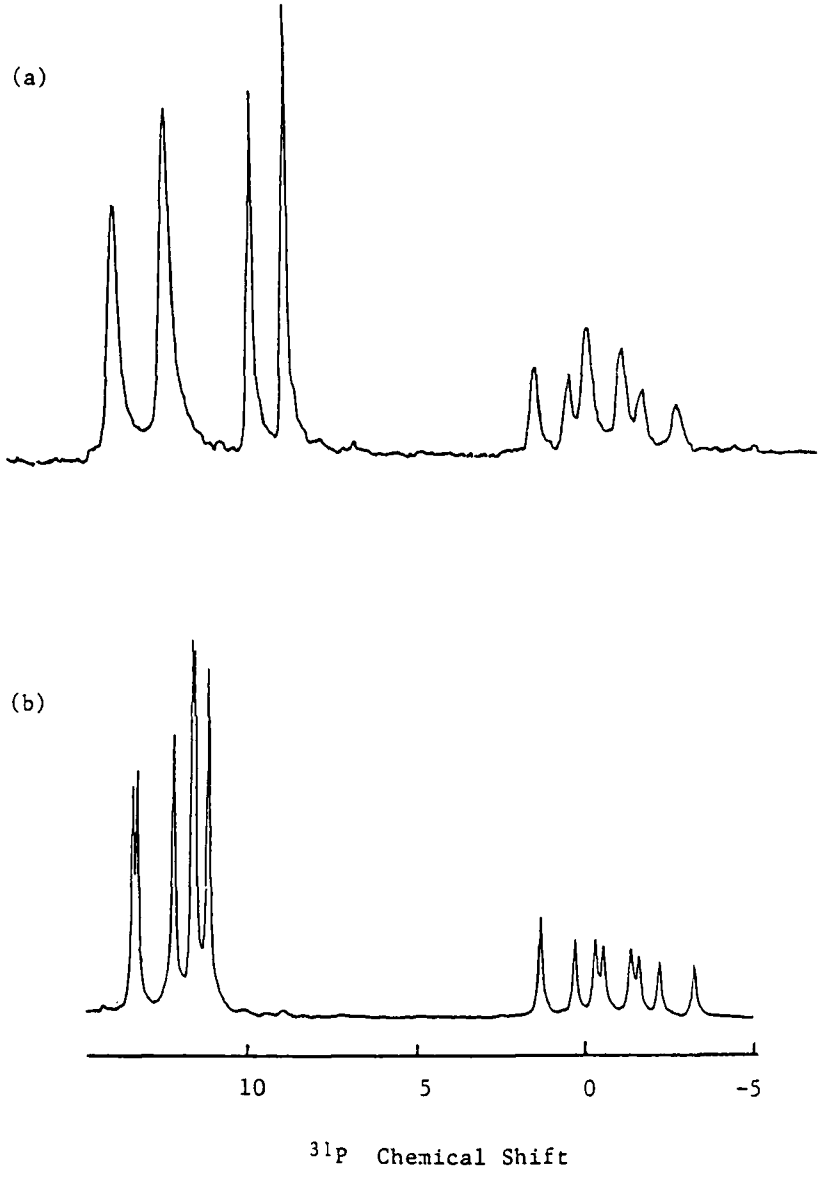


FIGURE 9 ^{21}P{H} NMR spectra of $N_3P_3(NPPh_3)(NH_2)Cl_4$(**2**) in acetone at 24.15 MHz (a) at room temperature, (b) at −85°C.

that in solution its preferred conformation is close to Type II. It is possible that the Type III, which it exhibits in the solid state may be due to the effect of its hydrogen-bonded structure, though it cannot be ruled out that Type III conformation also has $^4J(P, P)$ values close to zero.

We have observed differential chemical shifts on cooling. Thus in $N_3P_3(NPPh_3)(NH_2)Cl_4$ (**2**) the signals due to the PCl_2 and the $NPPh_3$ groups move closer together on cooling (Figure 9).

We have observed analogous effects with compounds containing the $N_3P_3Ph_2$ grouping and have reported these at this Symposium.[24] This phenomenon seems to be related to the presence of phenyl groups.

ACKNOWLEDGMENTS

J.K.F. is indebted to I.L.E.A. for same day release. M.B.H. and L.S.S. thank the S.E.R.C. for the provision of crystallographic equipment. R.A.S. is grateful to the Shin Nisso Kako Co. Ltd. for gifts of $N_3P_3Cl_6$, and to the University of London Intercollegiate Research Service for some NMR and mass spectrometric measurements.

REFERENCES

1. R. A. Shaw, *Phosphorus and Sulfur*, **5**, 363 (1979).
2. M. Biddlestone, S. N. Nabi and R. A. Shaw, *J. Chem. Soc., Dalton Trans.*, **1975**, 2634.
3. M. Biddlestone, R. Keat, H. Rose, D. S. Rycroft and R. A. Shaw, *Z. Naturforsch.*, **31b**, 1001 (1976).
4. M. Biddlestone, R. Keat, H. G. Parkes, H. Rose, D. S. Rycroft and R. A. Shaw, *Phosphorus and Sulfur*, 1985, in the press.
5. S. S. Krishnamurthy, P. Ramabrahmam, R. A. Shaw, A. R. Vasudeva Murthy and M. Woods, *Z. Anorg. Allg. Chem.*, in the press.
6. M. Biddlestone, R. A. Shaw, G. J. Bullen and P. E. Dann, *J. Chem. Soc., Chem. Commun.*, **1974**, 56.
7. Y. S. Babu, T. S. Cameron, S. S. Krishnamurthy, H. Manohar and R. A. Shaw, *Z. Naturforsch.*, **31b**, 999 (1976).
8. Y. S. Babu, H. Manohar, T. S. Cameron and R. A. Shaw, *Z. Naturforsch.*, **33b**, 682 (1978).
9. Y. S. Babu, H. Manohar and T. S. Cameron, *Acta Crystallogr.*, **B35**, 1410 (1979).
10. Y. S. Babu and H. Manohar, *Acta Crystallogr.*, **B35**, 2363 (1979).
11. Y. S. Babu, H. Manohar and R. A. Shaw, *J. Chem. Soc., Dalton Trans.*, **1981**, 599.
12. M. Krishnaiah, L. Ramamurthy, P. Ramabrahmam and H. Manohar, *Z. Naturforsch.*, **36b**, 765 (1981); H. Manohar, personal communication.
13. H. R. Allcock, K. D. Lavin, G. H. Riding and R. R. Whittle, *Organometallics*, **3**, 633 (1984).
14. V. Chandrasekhar, P. Ramabrahmam and H. Manohar, personal communication
15. R. Keat, M. C. Miller and R. A. Shaw, *J. Chem. Soc. (A)*, **1967**, 1404.
16. J. K. Fincham, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen) and R. A. Shaw, *J. Chem. Soc., Chem. Commun.*, 1985, 252.
17. J. K. Fincham, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen) and R. A. Shaw, this Symposium.
18. J. K. Fincham, M. B. Hursthouse, L. S. Shaw (née Gözen) and R. A. Shaw, unpublished results.
19. R. A. Shaw, *Pure and Applied Chem.*, **44**, 317 (1975).
20. *Idem*, *Z. Naturforsch.*, **31b**, 641 (1976).
21. *Idem*, *Phosphorus and Sulfur*, **5**, 363 (1979).
22. M. J. Begley, D. B. Sowerby and T. T. Bamgboye, *J. Chem. Soc., Dalton Trans.*, **1979**, 1401.
23. R. A. Shaw, Plenary lecture, this Symposium.
24. W. F. Deutsch, N. Gündüz, T. Gündüz, M. B. Hursthouse, E. Kilic, H. G. Parkes, L. S. Shaw (née Gözen), R. A. Shaw and M. Tüzün, this Symposium.