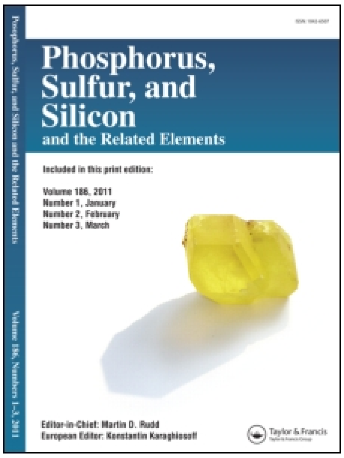


**Phosphorus, Sulfur, and Silicon and the Related Elements**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

# THE REACTIONS OF $N_3P_3CL_6$ WITH POLYFUNCTIONAL REAGENTS

Homaid A. Al-madfa[a]; Michael B. Hursthouse[b]; Harold G. Parkes[a]; 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.

**To cite this Article** Al-madfa, Homaid A. , Hursthouse, Michael B. , Parkes, Harold G. , Shaw (Née Gözen), Leyl S. and Shaw, Robert A.(1986) 'THE REACTIONS OF $N_3P_3CL_6$ WITH POLYFUNCTIONAL REAGENTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 28: 1, 203 — 211

**To link to this Article: DOI:** 10.1080/03086648608072810

**URL:** http://dx.doi.org/10.1080/03086648608072810

*Phosphorus and Sulfur*, 1986, Vol. 28, pp. 203–211
0308-664X/86/2802-0203/$15.00/0

# THE REACTIONS OF $N_3P_3Cl_6$ WITH POLYFUNCTIONAL REAGENTS

HOMAID A. AL-MADFA,[a] MICHAEL B. HURSTHOUSE,[b]
HAROLD G. PARKES,[a] 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.*

The reactions of $N_3P_3Cl_6$ with polyfunctional reagents, such as glycerol, are reported. NMR spectroscopic and X-ray crystallographic studies will be presented.

The reactions of $N_3P_3Cl_6$ and its derivatives with difunctional reagents have been widely explored synthetically, spectroscopically and crystallographically. (For summaries of the literature see refs. 1 and 2.) Four types of products have been obtained with aliphatic reagents: spiro, ansa, bridging and dangling (monofunctional) (**1**–**4**) (Figure 1).

By contrast the reactions of $N_3P_3Cl_6$ with trifunctional or higher functional reagents, which have been studied, are very few and have been the preserve of Labarre's group in Toulouse. Thus the reaction of $N_3P_3Cl_6$ with the trifunctional triamine spermidine, $H_2N(CH_2)_3NH(CH_2)_4NH_2$, was reported to give a unique product.[3] Various spiro, bridging and dangling, but not ansa, structures were considered.[4] Of these only two (**5**) and (**6**) (Figure 2) conformed to the mass spectrometric and analytical results. X-Ray crystallography proved the compound to be (**5**).

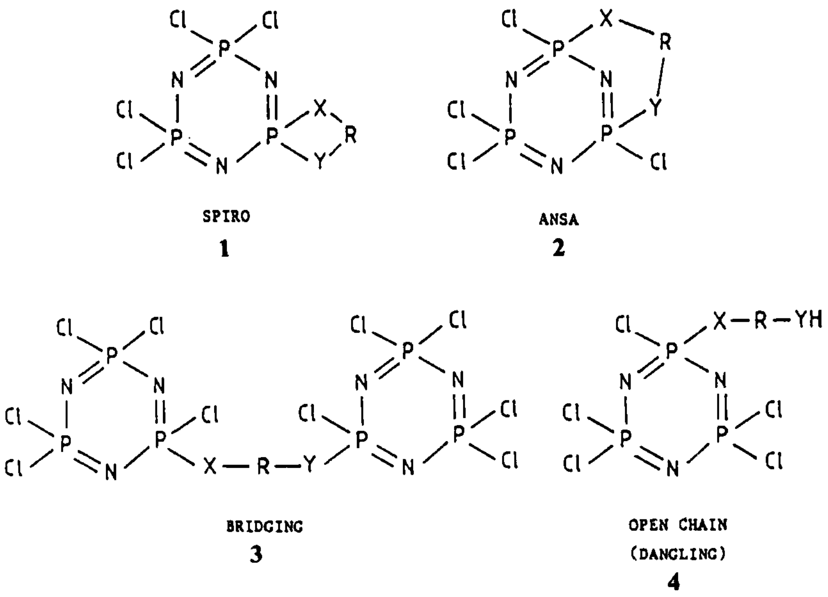
Compound (**5**) has one $N_3P_3$ ring with a six-membered spiro ring, with the third amino group forming a bridge to a second $N_3P_3$ fragment.[3,4] The isomer with a seven-membered spiro ring and a bridging structure (**6**) was not reported.[3,4] Evidently the formation of the six-membered spiro ring is greatly favoured over that of the seven-membered spiro ring, the latter not being observed, although seven-membered spiro rings are well documented: viz. $N_3P_3[O(CH_2)_4O]Cl_4$[5], $N_3P_3[O(CH_2)_4NH]Cl_4$[6] and $N_3P_3[NH(CH_2)_4NH]Cl_4$.[7]

No compound was reported where spermidine behaved as a difunctional or monofunctional reagent, with one, respectively two, dangling amino groups.

The reactions of $N_3P_3Cl_6$ with spermine, $H_2N(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2$, a tetrafunctional tetra-amine was reported to give exclusively one product.[8] If one enumerates the possible reaction products considering only spiro, bridging and dangling derivatives, the situation is even more complex and seventeen structures can be visualized. The exclusive product reported and crystallographically ex-

---

*Author to whom all correspondence should be addressed.



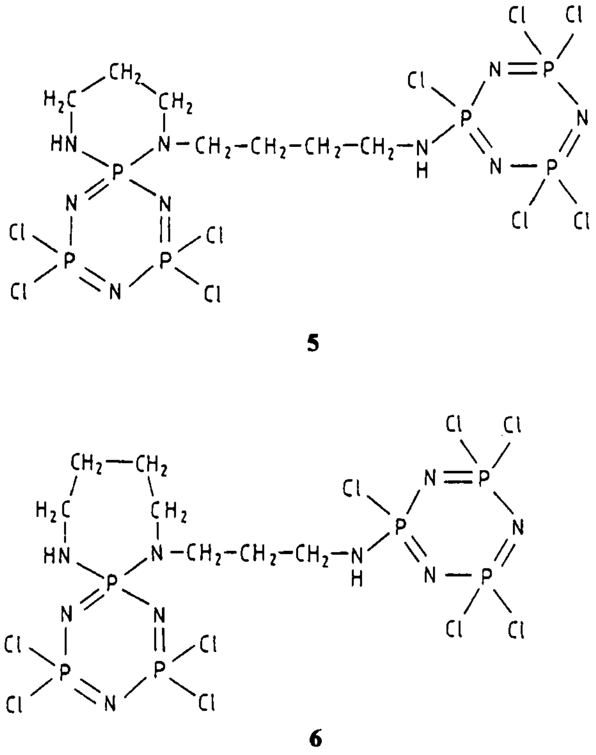
SPIRO
1

ANSA
2

BRIDGING
3

OPEN CHAIN
(DANGLING)
4

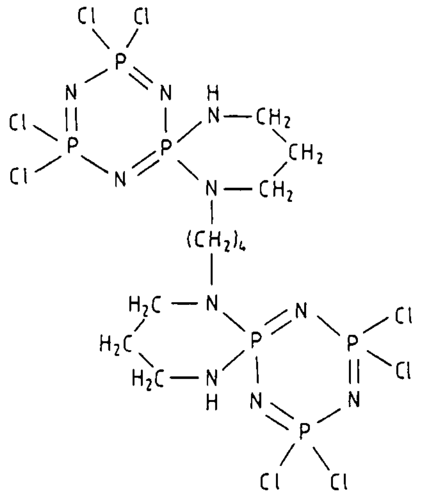
FIGURE 1 The four types of products of $N_3P_3$ derivatives with difunctional reagents.



5

6

FIGURE 2 The structure of the spermidine derivative of $N_3P_3Cl_6$.



**7**

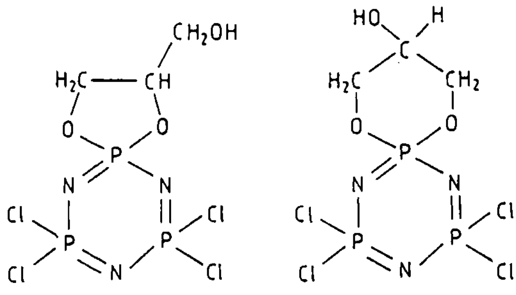
FIGURE 3 The structure of the spermine derivative of $N_3P_3Cl_6$.

amined[8] contains two $N_3P_3$ rings each with a six-membered spiro ring and these are linked by a $-(CH_2)_4-$ bridging unit (**7**) (Figure 3).

Again we note the preference to form six-membered rather than seven-membered spiro rings and the absence of dangling groups.

In view of our interest in the reactions of $N_3P_3Cl_6$ and derivatives with diols,[5,9-15] we have extended our investigation to glycerol, a triol.

From the reaction of $N_3P_3Cl_6$ with glycerol in the presence of tertiary base (pyridine) as HCl acceptor in the ratio of 2 : 1 : 3, we have isolated so far two products (**8**) and (**9**). The first (**8**) has so far not crystallised. Its mass spectrum gave a parent ion peak at 348 with an isotope pattern typical of four chlorine atoms. Hydroxy compounds are known to dehydrate ($-18$) and pick up a proton ($+1$).[16,17] Hence if we add 17 to the parent ion we obtain a mass number of 365. This corresponds to $N_3P_3(O_2C_3H_6)^{35}Cl_4$. Two isomer structures (**8a**) and (**8b**) would fit this formula (Figure 4).



**8a** **8b**

FIGURE 4 The two possible isomeric structures of compound (**8**).

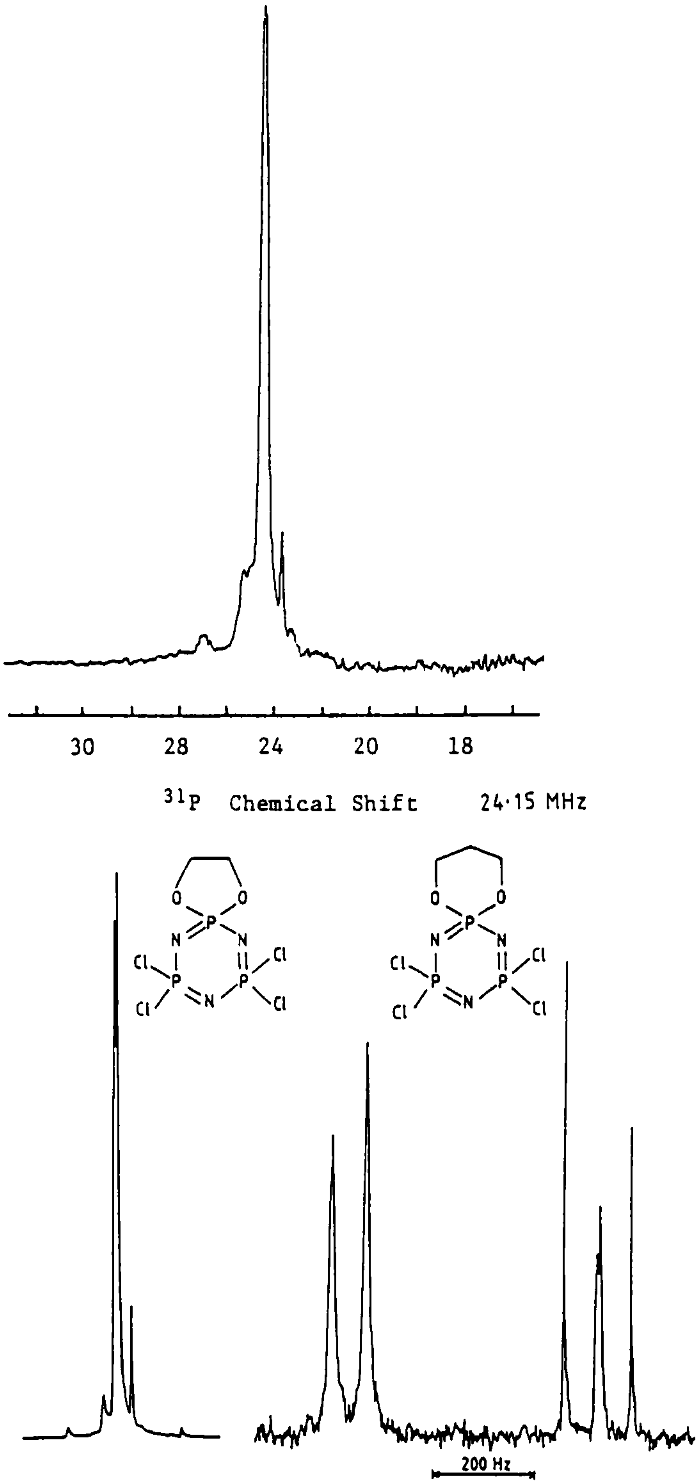


FIGURE 5 The $^{31}P$ {$^{1}H$} NMR spectrum of compound (8).

The $^{31}P$ NMR spectrum allows a distinction to be made between these two structures. Compound (**8a**) contains a five-membered spiro ring and hence it is analogous to $N_3P_3[O(CH_2)_2O]Cl_4$, (**10**) whilst the isomer (**8b**) has a six-membered ring and is analogous to $N_3P_3[O(CH_2)_3O]Cl_4$. (**11**).

The spectrum of compound (**8**) at 24.15 MHz is shown in Figure 5 and compared with those of $N_3P_3[O(CH_2)_2O]Cl_4$ and $N_3P_3[O(CH_2)_3O]Cl_4$ at the same field strength.

Clearly compound (**8**) resembles closely the five-membered prototype and hence we assign it structure (**8a**).

We obtain further evidence for the structure of (**8**) from its $^{13}$ C NMR spectrum. Inspection of structures (**8a**) and (**8b**) and comparison with related compounds reported elsewhere in this Symposium suggests that we should have three environments for structure (**8a**), two of these (part of the five-membered ring) and one dangling group. Structure (**8b**) on the other hand should show only two environments, (two identical carbon nuclei) as in other six-membered spiro rings. The oily compound (**8**) gave a $^{13}C$ NMR spectrum showing three environments, thus confirming structure (**8a**) (Figure 6).

The second compound (**9**) we have isolated is crystalline, m.p 99–100 °C. Its mass spectrum gives a parent ion at 674. This corresponds to $N_6P_6(O_2C_3H_5)^{35}Cl_9$. Two isomeric compounds would have this composition (**9a**) and (**9b**) (Figure 7).

In both compounds the two different $N_3P_3$ moieties should absorb independently of each other in a $^{31}P$ NMR spectrum. The spectrum (Figure 8) resembles a superposition of that of (**8a**) and of $N_3P_3Cl_5(OEt)$ (**12**).[18]

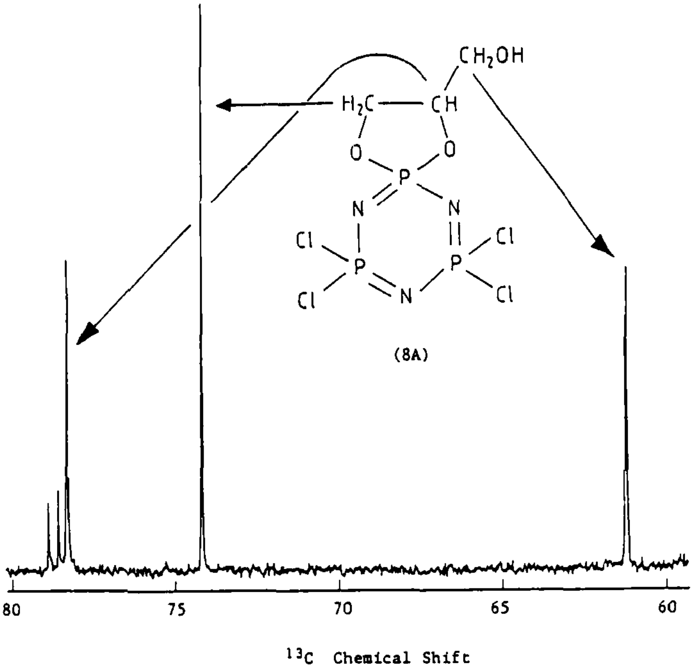
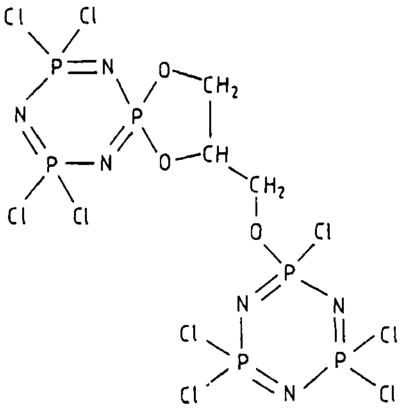
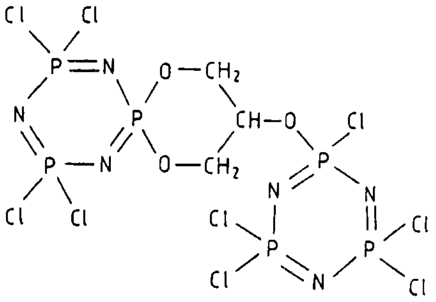


FIGURE 6 The $^{13}C$ $\{^1H\}$ NMR spectrum of compound (**8**).



**9a**



**9b**

FIGURE 7 The two possible isomeric structures of compound (**9**).

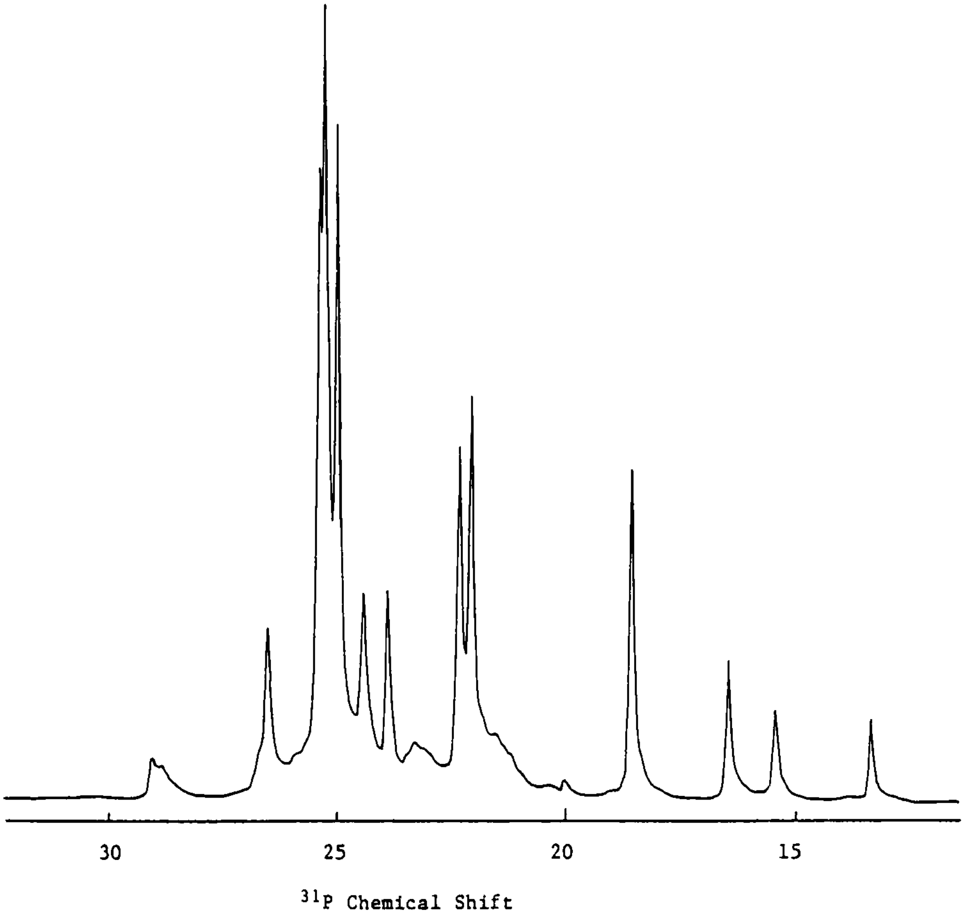


FIGURE 8 The $^{31}P$ $\{^{1}H\}$ NMR spectrum of compound (**9**).

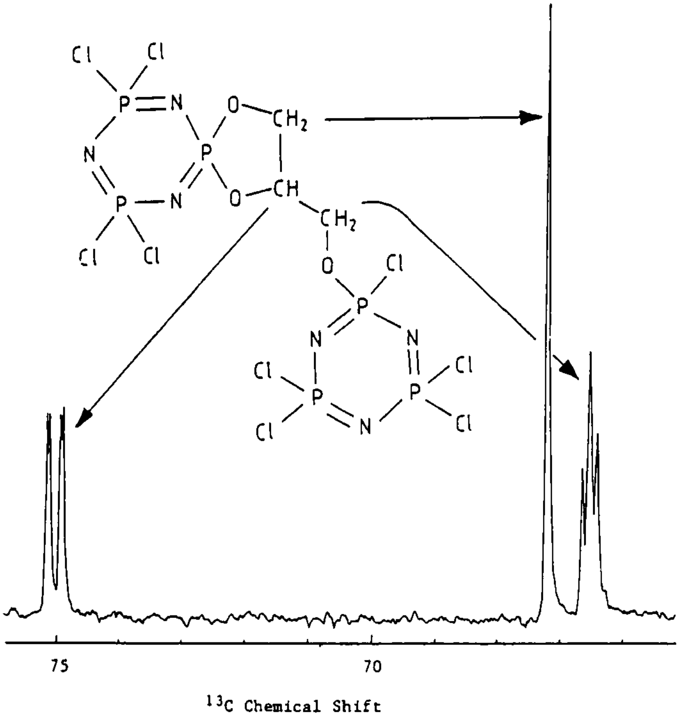


FIGURE 9 The $^{13}C$ $\{^1H\}$ NMR spectrum of compound (9).

Hence we assign to compound (**9**) structure (**9a**). Compound (**9**) gave an excellent $^{13}C$ NMR spectrum. It too showed three environments and this together with its phosphorus-carbon spin-spin coupling (Figure 9) clearly pointed to structure (**9a**).

To confirm our NMR deductions on the structure of compound (**9**), we endeavoured to carry out an X-ray crystallographic structure determination. This compound generally gave crystals unsuitable for crystallographic purposes, but we eventually grew some adequate ones from light petroleum.

The crystal structure conclusively established that the crystalline compound has structure (**9a**) (Figure 10).

The structure of (**9a**) has a very interesting and novel feature in that the two $N_3P_3$ rings are almost parallel to each other. We have thus obtained two new types of products from a trifunctional reagent. Both contain five-membered rather than six-membered rings. Compound (**8a**) is also the first example of a trifunctional reagent with a dangling group.

Our findings differ from those observed with the trifunctional amines, spermine[8] and spermidine,[3] where six-membered ring formation was favoured over seven-membered ring formation and no dangling groups were observed.

With sugars and other polyols it is well established that in acetal formation five-membered rings are favoured kinetically, whilst six-membered rings are favoured thermodynamically. We are currently investigating whether this pertains also to our system.

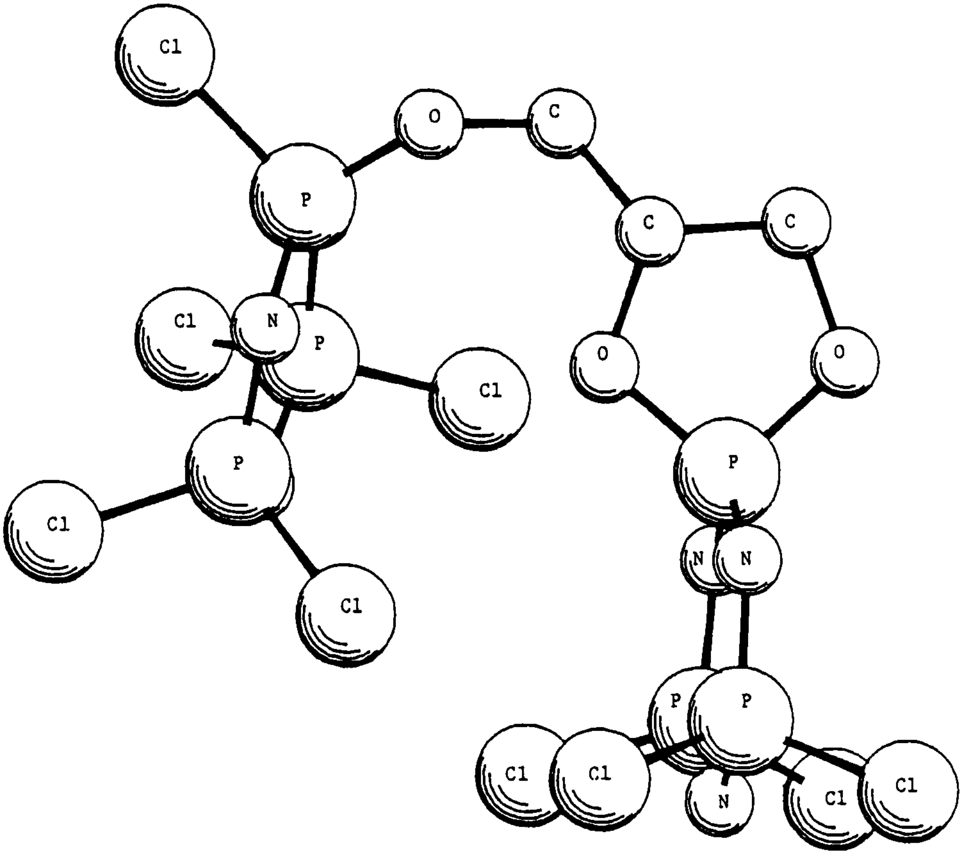


FIGURE 10 The molecular diagram of compound (9).

## ACKNOWLEDGMENTS

H.A.A-M. wishes to thank the University of Qatar for a post-graduate studentship. 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. A. H. Alkubaisi, W. F. Deutsch, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen) and R. A. Shaw, this Symposium.
2. A. H. Alkubaisi, H. A. Al-Mafda, W. F. Deutsch, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen) and R. A. Shaw, this Symposium.
3. G. Guerch, J-F. Labarre, R. Enjalbert, J. Galy and J. P. Declercq, *Inorg. Chim. Acta.*, **83**, L33 (1984).
4. G. Guerch, Ph.D. Thesis, Paul Sabatier University, Toulouse, France, December 2, 1983.
5. S. R. Contractor, M. B. Hursthouse, L. S. Shaw (née Gözen), R. A. Shaw and H. Yilmaz, *Acta Crystallogr.*, **B41**, 122 (1985).
6. H. G. Parkes and R. A. Shaw, unpublished results.

7. G. Guerch, J-F. Labarre, R. Roques and F. Sournies, *J. Mol. Struct.*, **96**, 113 (1983).
8. J-F. Labarre, G. Guerch, F. Sournies, R. Lahana, R. Enjalbert and J. Galy, *J. Mol. Struct.*, **116**, 75 (1984).
9. S. R. Contractor, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen), R. A. Shaw and H. Yilmaz, *Phosphorus and Sulfur*, **18**, 149 (1983).
10. S. R. Contractor, M. B. Hursthouse, L. S. Shaw (née Gözen), R. A. Shaw and H. Yilmaz, *ibid.*, p. 421.
11. S. R. Contractor, Ph.D. Thesis, London, 1983.
12. S. R. Contractor, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen), R. A. Shaw and H. Yilmaz, *J. Chem. Soc. Chem. Commun.*, **1984**, 675.
13. S. R. Contractor, M. B. Hursthouse, H. G. Parkes, L. S. Shaw (née Gözen), R. A. Shaw and H. Yilmaz, this Symposium.
14. 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.
15. S. R. Contractor, H. B. Parkes, R. A. Shaw and H. Yilmaz, unpublished results.
16. D. H. Williams and I. Howe, Principles of Organic Mass Spectrometry, McGraw-Hill, London, 1972, p. 116.
17. F. W. McLafferty, Interpretation of Mass Spectra, 3rd Edn., University Science Books, Mill Valley, California, 1980, p. 166.
18. F. Heatley and S. M. Todd, *J. Chem. Soc.*, *(A)*, 1966, 1152.