

have all been observed. An important aspect of the recent studies is that the polyynes as well as C_3N and C_4H seem to be particularly abundant in the expanding gaseous envelope which surrounds the cool carbon star IRC + 10216.¹⁰³

5 Discussion

There are a few general points that seem to be worth making in this summary.

Microwave spectroscopy is a technique which has in the past been rather difficult to apply* and in general has been used by chemical physicists to make detailed studies of molecular structure and other molecular parameters such as those obtainable from vibration-rotation analysis. It is, however, a very flexible technique and in recent years a few groups have used it to make significant contributions to other areas: Oka to collisional energy transfer,¹²⁶ Legon and Millen to the study of weakly bound complexes,¹²⁷ Johnson and Lovas⁵⁶ as well as Hirota, Saito, and co-workers¹²⁸ to unstable molecules. Cross-field application of expertise is in general valuable. In this work the main philosophy has been to study problems of intrinsic chemical interest; essentially to use microwave spectroscopy, backed up synergistically by other techniques such as photoelectron spectroscopy, to carry out main group chemistry on compounds not accessible by standard chemical techniques. It has been traditional to hang on heavy groups in order to stabilize elusive moieties and *then* use the entity in further reactions. In the present approach, however, the aim has been to find a route to semi-stable species, characterize them and develop techniques for further reaction. The last aim is now being developed as shown by reactions such as (28) in which NCCP was made from HCP *on line*. It is probably worth noting that the very properties that are smothered by substituent group stabilization may be the most valuable that these moieties have. Indeed, it is probably the differences between related species rather than their similarities that are most important and likely to lead to new chemistry. To force them into some pre-ordained mould may by-pass important features.

The low-pressure operational conditions of the microwave and photoelectron techniques have been critical in slowing down the polymerization or decomposition rates sufficiently to facilitate detection. In retrospect there has been a subconscious tendency to avoid modifying the equipment and instead tailor experiments by, for instance, aposite precursor synthesis to exploit those virtues of the basic instrument that experience has uncovered. For instance, the microwave cell which consists of a 1 metre metal tube allowing (rather difficult) access only at the ends offers outstanding sensitivity. Although it is poor for the

* It will again become difficult to apply since Hewlett Packard, the only firm to market, successfully, a commercially viable instrument, no longer makes it.

¹²⁶ T. Oka, *Adv. At. Mol. Phys.*, 1973, 9, 127.

¹²⁷ J. W. Bevan, Z. Kisiel, A. C. Legon, D. J. Millen, and S. C. Rogers, *Proc. R. Soc. London, Ser. A*, 1980, 372, 441.

¹²⁸ E. Hirota, S. Saito, *et al.*, Annual Review, Institute for Molecular Science, Okazaki National Research Institutes, Japan, 1980, pp. 38–51; 1981, pp. 29–46.

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detection of free radicals, which decay too quickly, it is excellent for species of intermediate stability which last long enough effectively to fill a 1–2 metre active length at moderate flow rates.

Technical reasons have prevented the beautiful spectroscopic patterns from being displayed in early microwave studies. The data have, in the past, been presented as inedible tabulations of relatively large numbers which mask the patterns and preclude recognition. Indeed, it is the initial observation, together with abstract pattern recognition, which is the cathartic experience that drives this and many other types of research. As a consequence it has been a very important objective in this work that these patterns be displayed in the literature and in this review a range of textbook examples has been presented.

The general result of this work is that the chemistry of: $>C=S$, $>C=Se$, $-B=S$, $-B=Se$, $>C=P-$, and $-C\equiv P$ containing species has been either extended or initiated so that they can now take their place beside their well-studied first row counterparts, the carbonyls, imines, and nitriles and be considered as viable functional groups in their own right.

Some *specific* points about the various groups of molecules studied are discussed below.

A. Thiocarbonyls and Selenocarbonyls.—As far as thiocarbonyls are concerned they were the first group to be studied and were used to hone the experimental techniques. They were also rather easily handled, after all OCS is a well known species being, apart from the smell, rather well-behaved. Thiocarbonyls seem to be sufficiently close in stability to carbonyls that traditional chemistry can handle them except for the simplest ones such as $CH_2=S$. Even $Me_2C=S$ seems to be relatively stable. As well as the thiocarbonyls, the selenocarbonyls can also be studied though with somewhat more difficulty. The major technical problem is probably the incredible persistence of the smell and the apprehension with regard to selenium's reputation as a poison, a reputation almost entirely based on the properties of H_2Se . It is probably the close similarity between Se and S in organic configurations that is responsible for the blocking of metabolic pathways.

The results do indicate that with some modification of technique such molecules as $CH_2=S$ and $MeCH=S$ could be useful reactants with parallel chemical behaviour to the aldehydes and ketones.

B. Sulphidoboron Compounds.—It seems curious that oxoboron molecules seem to be *less* stable than the analogous sulphidoboron molecules. This is based on the circumstantial evidence that they have not been detected by the techniques that produced the sulphidoborons. The yields of the halides, especially CIBS, are excellent as witnessed by the p.e. data, but rather poor in the case of MeBS which presumably reflects the alternative reactions which the precursor may follow.

The structural data indicate that the B=S bond length is relatively constant at $1.604 \pm 0.004 \text{ \AA}$ for the analogues studied. The nitriles show a similar degree

of bond length inflexibility. MeBS presents the first example of a bond between sp^3 hybridized carbon and sp hybridized boron. An increase of 0.066 Å occurs in $r(\text{C}-\text{B})$ between MeBS and MeBF₂ where it is 1.534 Å and 1.60 Å respectively. This is in good agreement with the CIBS/CIBF₂ system where it increases from 1.681 Å in CIBS by 0.047 Å to 1.728 Å in CIBF₂.

The mechanism for producing sulphidoborons is probably complicated. Detailed searches have not yielded any evidence for XSB isomers which, if formed, would probably be too short-lived for our detection techniques. An alternative mechanism follows from known reactions of Cl₂S₂ and boron. Cl₂S₂ decomposes above 300 °C to form Cl₂ and sulphur, and boron reacts with Cl₂ and sulphur at elevated temperatures to form BCl₃ and B₂S₂. Further, it is known that BCl₃ reacts with B₂O₃ to form CIBO.¹²⁹ Thus, an alternative reaction, equation (32), is possible.



The photoelectron data on CIBS have provided circumstantial evidence for such a scheme in that large quantities of BCl₃ are produced at temperatures below those needed to form CIBS.

From the analysis of the quadrupole structure of CIBS an estimate of the character of the Cl—B bond can be obtained. This indicates that the bond has 0.5 σ character, 0.23 π character, and 0.27 ionic character.⁴⁸

An almost complete, apart from IBS, photoelectron correlation diagram can now be drawn as shown in Figure 14. This shows that for the $\pi(\text{B}=\text{S})$ system there is a gradual destabilization with substituent. The order of stability is: H > F > Cl > Br in line with an increase in electron density due to the effects of hyperconjugation. In the $\sigma(\text{B}=\text{S})$ system the introduction of F stabilizes this orbital in line with the expected withdrawing inductive effects. The effect of Cl and Br in this case is negligible.

Preliminary theoretical calculations indicate some interesting features about the XB=S system which relate to the question of whether there is a double or triple bond between boron and sulphur. There are two electrons in the $\sigma(\text{BS})$ orbital and four in the degenerate $\pi(\text{BS})$ orbitals, so one might expect a major contribution from a valence configuration such as $\text{XB}^-\equiv\overset{+}{\text{S}}$ implying a build-up of charge on the boron. This does not appear to be the case as the boron, at least according to preliminary Gaussian 70 calculations, is effectively uncharged. It turns out that the electron density in the π orbitals resides mainly on the sulphur atom and the two π bonds are roughly half-strength. The initial indication is that the net effect is roughly that of a double bond because the π orbitals have 50:50 bonding:non-bonding character.

C. Phospha-alkenes and Phospha-alkynes.—The results on phospha-alkenes and phospha-alkynes have shown that the family resemblance between P and N in multiple bond configurations is considerably closer than chemists realised. In fact

¹²⁹ J. Blauer and M. Forber, *Trans. Faraday Soc.*, 1962, **58**, 2090.

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it is somewhat surprising, in the light of such results as the ease of production of FCP and the stability of t-BuCP as well as the big hints implicit in the existence of $\text{HC}\equiv\text{P}$ and phosphabenzene, that the field did not open up much sooner. The reason for the lack of awareness was probably the fact that these compounds are *just* past the threshold of attack by traditional chemical techniques. They are *only just* past this threshold as such molecules as MeCP can be retrieved after trapping, but this is not the case for the sulphidoborons which appear to form trimers before revaporizing.

In these experiments there has also been no evidence for isomers of the form XPC analogous to the isonitriles.

From the general structural study one can obtain the following covalent radii for phosphorus.

	P	C	Sum		
<i>sp</i>	0.94	0.60	1.54	Å	$\text{CH}_3\text{C}\equiv\text{P}$
<i>sp</i> ²	1.00	0.67	1.67	Å	$\text{CH}_2=\text{PH}$
aromatic <i>sp</i> ²	1.03	0.70	1.73	Å	$\text{C}_5\text{H}_5\text{P}$
<i>sp</i> ³	1.07	0.77	1.84	Å	CH_3PH_2

The photoelectron data indicate that the $\pi(\text{C}\equiv\text{P})$ orbital is the HOMO which fits in nicely with the fact that π -complexes such as the Pt compound, Figure 22, can be made. In the case of HCN the σ and π orbitals have almost identical ionization energies in line with the co-ordinating properties of nitriles. In some respects, particularly in its co-ordinating ability, $\text{HC}\equiv\text{P}$ behaves more like $\text{HC}\equiv\text{CH}$ than $\text{HC}\equiv\text{N}$.

D. Multiply Bonded Si.—An important series of molecules represented on the CH_2O cube in Figure 1 has not featured in the experimental work summarized in previous sections. The sila-alkene family related to $\text{CH}_2=\text{SiH}_2$ is absent, though not for want of trying. As pointed out in Section 1, the techniques applied have not in general involved the custom construction of equipment designed to catch very elusive species (*i.e.* species with lifetimes of *ca.* 10^{-3} – 10^{-6} s) but rather are aimed at those which are just fickle (*i.e.* lifetimes of *ca.* 1 s). Our experiments on $\text{Si}=\text{X}$ species have indicated that they have very elusive spirits indeed, with reactivities comparable with those of small free radicals.

The family resemblance between C and Si is very much less obvious and the generation gap that exists is perhaps most spectacularly exemplified by the difference between a sample of CO_2 and a sample of SiO_2 .

The reluctance of $\text{Si}=\text{X}$ species to submit to the techniques of Section 2 led to a theoretical study of the problem as a last resort.^{130,131} This showed that Si has a strong tendency to remain *divalent* which manifests itself critically during attempts to produce multivalent configurations. This tendency is experimentally apparent in the relative stability of SiF_2 compared with that of CF_2 , which readily forms $\text{CF}_2=\text{CF}_2$.

¹³⁰ J. N. Murrell, H. W. Kroto, and M. F. Guest, *J. Chem. Soc., Chem. Commun.*, 1977, 619.

¹³¹ H. W. Kroto, J. N. Murrell, A. Al-Derzi, and M. F. Guest, *Astrophys. J.*, 1978, **218**, 886.

Some early results of Gusel'nikov and Flowers¹³² presented circumstantial evidence for $>\text{Si}=\text{C}<$ type intermediates in pyrolysis experiments on cyclic silaethenes. More recently Brookes *et al.*¹³³ have succeeded in using large stabilizing groups to form such molecules as $(\text{Me}_3\text{Si})_2\text{Si}=\text{C}(\text{OSiMe}_3)$ adamantyl which has been characterized by X-ray analysis. A very interesting result was obtained by Leclercq and Dubois¹³⁴ who detected the transient species $\text{CH}_2=\text{Si}$ during flash discharge experiments in MeSiH_3 . This observation is in circumstantial agreement with the theoretical prediction that Si prefers to be divalent and that in this case $\text{CH}_2=\text{Si}$ is much more stable than $\text{HC}\equiv\text{SiH}$.¹³⁰ This study also indicates that $\text{HN}=\text{Si}$ is much more stable than $\text{HSi}\equiv\text{N}$, which is of course a reversal of the HNC/HCN situation.^{130,131}

E. Poly-yne.—The original reason for studying the poly-yne lay in their simplicity and the consequent tractability of their rotational spectra. In addition their dynamic behaviour should be simpler than that manifested by other molecules. The spectra and the basic analysis have already been discussed and the resulting data show some interesting points. The accurate structural study Table 6 provides a textbook example of delocalization in extended conjugated systems. As the conjugated system extends from HC_3N to HC_5N delocalization increases the lengths of the triple bonds and decreases the lengths of the single bonds, especially near the middle of the chain. For instance $r(\text{C}\equiv\text{C})$ increases from 1.205 Å for HC_3N to 1.2225 Å for HC_5N . The bond lengths show a general trend which is manifested by the success of the extrapolation technique used by Oka to estimate the B_0 values (previous section). A second indicator of good behaviour is the excellent transferability of structural data. This has recently been shown by $\text{N}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}\equiv\text{P}$ whose experimental B_0 value was found to be 873.480 MHz.⁸⁵ This can be compared with an estimated value of 873.66 MHz based on $[\text{N}\equiv\text{C}-\text{C}\equiv\text{C}]$ lengths taken directly from the appropriate part of HC_5N and a $[\text{C}-\text{C}\equiv\text{P}]$ structure taken from that of $\text{N}\equiv\text{C}-\text{C}\equiv\text{P}$.

The vibration-rotation analysis for such species is clearly quite severe as indicated by Figures 25 and 30. An analysis for HC_5N has been carried out which has shown that the transitions involving highly excited vibrational modes are well explained by the standard theory which governs general vibration-rotation behaviour.¹⁰⁹ This was a little surprising as the instinctive feeling is that molecules in such states are very bent systems on average, and that a theory based, as this was, on a small amplitude approximation might show signs of breakdown.

F. Interstellar Poly-yne.—The origin of interstellar molecules has been the subject of numerous studies and radio observations have instigated much

¹³² L. E. Gusel'nikov and M. C. Flowers, *J. Chem. Soc., Chem. Commun.*, 1967, 864.

¹³³ A. G. Brook, F. Abdesaken, B. Gutekunst, G. Gutekunst, and R. K. Kallury, *J. Chem. Soc., Chem. Commun.*, 1981, 191.

¹³⁴ H. Leclercq and I. Dubois, *J. Mol. Spectrosc.*, 1979, 76, 39.

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recent work. In particular, gas phase ion-molecule reactions and grain surface catalysis have been invoked. The detection of long chains, however, has presented severe problems to the acceptance of these processes. It is certainly not clear that ion-molecule reactions can build up such chains preferentially with respect to branched species, especially as branched ions are generally expected to be more stable. Indeed, if there are analogous, branched hydrocarbon species in commensurate numbers with the C_n chain molecules, the clouds must contain significantly more molecules than ever considered possible. It is also not at all clear that the chains can be formed on grains as it is seemingly impossible for them to desorb at the low temperatures that exist in clouds such as TMC1 (ca. 10–30 K). The chemistry is not clear but the most recent results do indicate that some molecules are formed in the envelopes of cool stars. The cool star IRC+10216, which has a high carbon to oxygen ratio, has now been shown to be pumping out molecules, in particular the chains. In addition, it seems to be pumping out grains. It may well be that in these stars grains and chains are formed at roughly the same time but whether there are enough of these stars to account for the colossal quantities of molecules now known to exist is not clear.

Suffice it to say, the interstellar studies have shown that some very long molecules exist in the space between the stars. They may be very long indeed and their relationship with grains is far from being understood. In fact, it is only now that a possible relationship can even be contemplated.¹⁰³ The long chains may be an intermediate form of carbon, between atoms and small molecules such as C, C_2 , and C_3 , which are well known, and particles with high carbon content such as soot. Another factor is that chains of this length must be good scatterers of radiation due to their electronic properties and so it is even possible that they are the grains.¹⁰³ Douglas has suggested that the chains give rise to the so-called Diffuse Interstellar Lines.¹³⁵ These are a set of some 40 broad interstellar features in the visible spectroscopic region which have perplexed astronomers for nearly 50 years.

The latest data indicate that some new experimental and theoretical work on the mechanism of precipitation of particles from carbon vapour is necessary. The interaction of radiation with these chains also should be studied to see how it might relate to the quantitative interstellar scattering characteristics.

Finally, the interesting general point is that these molecular clouds are the raw material out of which stars and particularly planets form. The mechanism of planet formation is still far from clear and indeed the relationship of the molecules in these clouds with those in the earth's atmosphere is even less clear. We now know that molecules are formed in stars and pushed out into space. There are now, therefore, three known ways in which bio-emotive molecules, such as glycine, can be formed: (1) in the biosphere by Urey-Miller type processes; (2) in the cold interstellar clouds by ion-molecule reactions and perhaps also by grain catalysed processes; (3) in reactions in circumstellar shells.

¹³⁵ A. E. Douglas, *Nature*, 1977, **269**, 130.

There is clearly an inexorable drive to form the molecules that are the building blocks of life. Indeed, the new results suggest that one should consider whether the circumstellar molecules might actually have survived the transition from circumstellar shell to the molecular cloud, protected from photolysis by starlight in a symbiotic relationship with the grains, and perhaps accreted into planetary atmospheres more or less intact during a later cooler phase of planet formation. The new results herald a new look at not only the origin of the biosphere but also a new look at the mechanism of grain formation and grain identity, as well as the formation of larger objects such as planets.

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