

Received: November 22, 1983; accepted: November 30, 1982

ON THE STRUCTURAL EFFECTS OF CF<sub>3</sub> GROUPS\*

HEINZ OBERHAMMER

Institut für Physikalische und Theoretische Chemie, Universität  
Tübingen, 7400 Tübingen (F.R.G.)

SUMMARY

Based on gas phase molecular structures for a series of molecules containing CF<sub>3</sub> groups, some general effects of these groups on the molecular geometries are observed. Three aspects of such effects are discussed: (1) the CH<sub>3</sub>/CF<sub>3</sub> substitution effect on bond lengths, (2) steric effects of CF<sub>3</sub> groups as compared to other substituents (F, Cl, CH<sub>3</sub>) and (3) the effect of CF<sub>3</sub> groups on the stereochemistry of trigonal bipyramidal molecules.

INTRODUCTION

CF<sub>3</sub> groups are the most widely used substituents in fluorine chemistry, beside fluorine itself, of course. Since geometric structures and their changes upon substitution can give us some insight into the bonding properties of a molecule, it may be profitable to study the effects, such CF<sub>3</sub> groups have on the geometric structures, by comparing CF<sub>3</sub> compounds with analogous molecules. The data used for this comparison will be restricted to gas phase studies for two reasons: (1) most CF<sub>3</sub> compounds are highly volatile and (2) gas phase data represent the structure of the free molecule, i.e. unperturbed by neighbouring molecules, crystal effects, lattice vibrations etc. Gas phase structures, therefore, allow a direct correlation with bonding properties. There are essentially two methods available

---

\*Paper delivered at 10th International Symposium on Fluorine Chemistry, Vancouver, B.C., Canada, August 1982.

for gas phase studies, microwave spectroscopy and gas electron diffraction. Microwave spectroscopy by itself is not very adequate for studying fluorine compounds, since there exist no fluorine isotopes except  $^{19}\text{F}$ . Consequently, a limited number of  $\text{CF}_3$  compounds - less than ten - have been studied by this method. A larger number - close to sixty - have been investigated by electron diffraction, although there are considerably less systematic studies known in the literature.

We shall consider here three different structural effects of  $\text{CF}_3$  groups, the effect on bond lengths as compared to analogous methyl compounds, steric effects of  $\text{CF}_3$  groups compared to other ligands, such as fluorine, chlorine or methyl and the effect of  $\text{CF}_3$  groups on the stereochemistry of trigonal bipyramidal molecules.

#### $\text{CH}_3/\text{CF}_3$ SUBSTITUTION EFFECT ON BOND LENGTHS

		$\Delta r = r_{\text{CF}_3} - r_{\text{CH}_3}$
$\text{H} \text{---} \frac{1.099}{\text{---}} \text{---} \text{CH}_3$	$\text{H} \text{---} \frac{1.102}{\text{---}} \text{---} \text{CF}_3$	+ 0.003
$\text{J} \text{---} \frac{2.139}{\text{---}} \text{---} \text{CH}_3$	$\text{J} \text{---} \frac{2.138}{\text{---}} \text{---} \text{CF}_3$	- 0.001
$\text{Br} \text{---} \frac{1.939}{\text{---}} \text{---} \text{CH}_3$	$\text{Br} \text{---} \frac{1.923}{\text{---}} \text{---} \text{CF}_3$	- 0.016
$\text{Cl} \text{---} \frac{1.781}{\text{---}} \text{---} \text{CH}_3$	$\text{Cl} \text{---} \frac{1.752}{\text{---}} \text{---} \text{CF}_3$	- 0.029
$\text{F} \text{---} \frac{1.385}{\text{---}} \text{---} \text{CH}_3$	$\text{F} \text{---} \frac{1.319}{\text{---}} \text{---} \text{CF}_3$	- 0.066

Fig. 1.  $\text{CH}_3/\text{CF}_3$  substitution effect in  $\text{XCF}_3$  compounds [1].

For this first aspect we have the largest amount of structural data available and we shall start with the most simple examples, *i.e.*  $\text{XCF}_3$  compounds with X being a single atom (Fig. 1). For the electropositive hydrogen the bond length increases slightly, in the case of iodine with an electronegativity equal to that of carbon there is no effect on the C-I bond length within experimental error limits. For more electronegative X atoms the C-X bonds shorten and in the extreme case of fluorine this shortening is 0.066 Å upon  $\text{CH}_3/\text{CF}_3$  substitution.

A similar correlation between  $\text{CH}_3/\text{CF}_3$  substitution effect and electronegativity is observed for compounds containing two  $\text{CF}_3$  groups, such as selenide, sulfide and ether (Fig. 2). For the electropositive central atoms selenium and sulfur the bonds are longer in the  $\text{CF}_3$  compounds as compared to the methyl analogues, for the electronegative oxygen atom the effect is reversed, the C-O bond shortens upon  $\text{CH}_3/\text{CF}_3$  substitution.

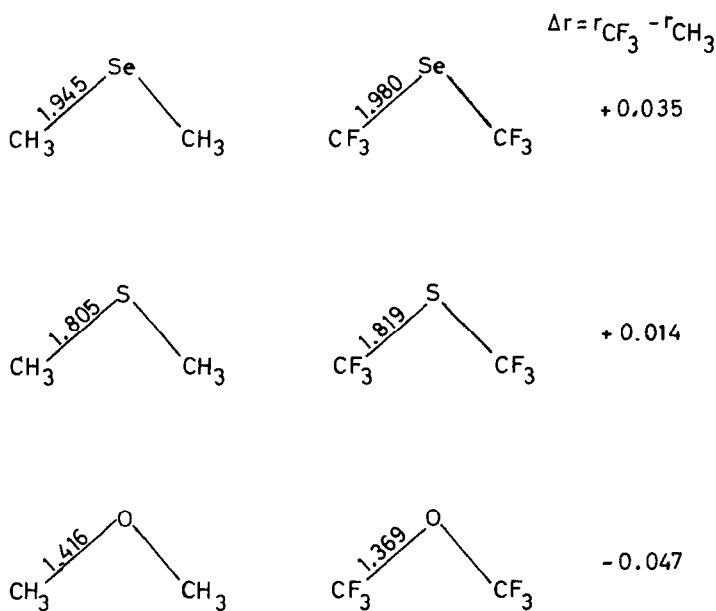


Fig. 2.  $\text{CH}_3/\text{CF}_3$  substitution effect in  $\text{X}(\text{CF}_3)_2$  compounds  
 [2 - 7].

A plot of the substitution effect ( $\Delta r$ ) in  $XCF_3$  compounds vs. the electronegativity of X shows a linear correlation. A negative value of  $\Delta r$  corresponds to bond shortening upon  $CH_3/CF_3$  substitution. In the case of two  $CF_3$  groups we find again a linear correlation between  $\Delta r$  and the electronegativity of the central atoms O, S and Se, but with a steeper slope, *i.e.* a stronger dependence on the electronegativity (Fig. 3). For compounds with three  $CF_3$  groups and central atoms N, P and As this slope is again steeper.

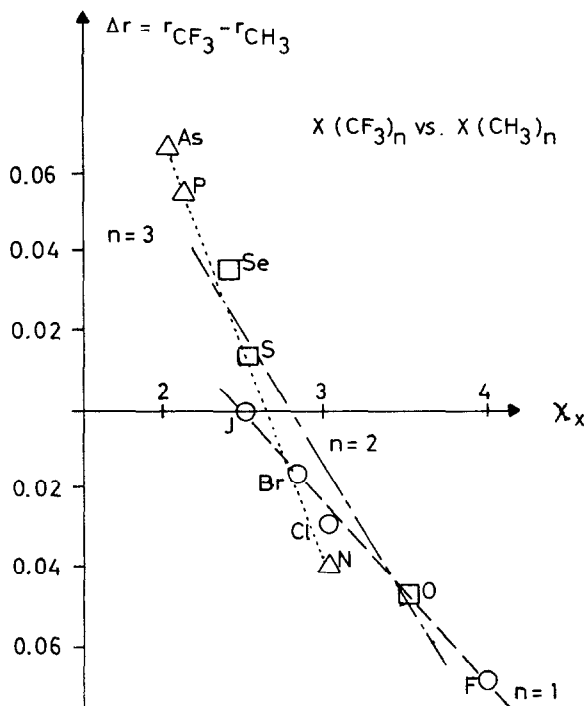


Fig. 3. Correlation between  $CH_3/CF_3$  substitution effect and electronegativity of central atom X in  $X(CF_3)_n$  ( $n=1,2,3$ ) compounds.

This correlation between substitution effect and electronegativity can be rationalized with a very simple concept based on electrostatic effects. For two extreme cases the atomic net charges from semiempirical CNDO/2 calculations are shown in

Fig. 4. In methyl fluoride the methyl carbon atom carries a small positive net charge and fluorine, of course, is negative. But the polar interaction - attractive in this case - is small. In tetrafluoromethane the carbon atom has a very high positive net charge and here the electrostatic attraction is high, causing strong shortening of the C-F bond. In trimethyl phosphine the methyl carbon atom carries again a small net charge which is negative in this case and phosphorus is slightly positive. Polar effects for the P-C bonds, however, are small. In the  $\text{CF}_3$  compound the carbon atoms carry again high positive charges, but now the electrostatic interactions are repulsive, since the electropositive phosphorus atom has a positive net charge.

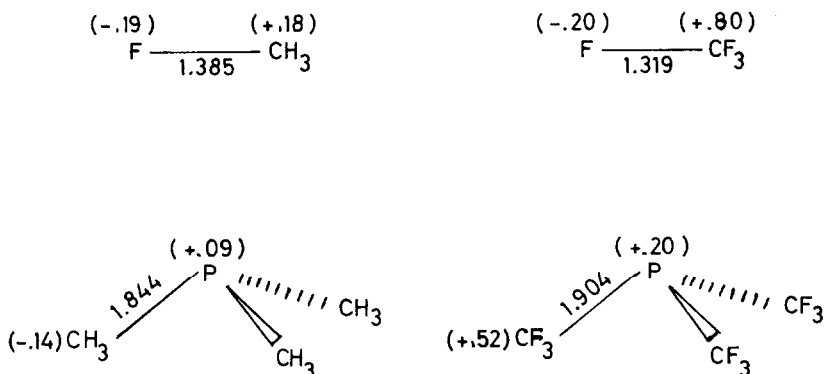


Fig. 4. Atomic net charges for  $\text{FCH}_3/\text{FCF}_3$  and  $\text{P}(\text{CH}_3)_3/\text{P}(\text{CF}_3)_3$ . (Bond distances in the phosphines see [8, 9]).

In general, methyl carbon atoms carry small net charges, positive or negative, depending on the central atom, and polar effects are negligible for methyl compounds. The  $\text{CF}_3$  carbon atoms, however, always have high positive net charges and polar effects are important in  $\text{CF}_3$  compounds. These polar effects are attractive and cause bond shortening for electronegative X atoms (F, O, N) and they are repulsive for electropositive X atoms (Se, P, As). In addition to these dominant polar effects the CNDO/2 calculations indicate in all cases a slight decrease in the covalent bond order for  $\text{CF}_3$  compounds [10].

The situation becomes more complicated for not uniformly substituted compounds and we shall discuss two examples, the first one with the electronegative central atom nitrogen. We recall that the N-C bonds in trimethylamine shorten upon  $\text{CH}_3/\text{CF}_3$  substitution, in perfect agreement with our concept. In tris(trifluoromethyl)amine the polar effect is very strong and attractive (Fig. 5). In difluoromethylamine, however, the effect is reversed and the N-C bond length increases when methyl is replaced by a  $\text{CF}_3$  group. The reason for this is the nitrogen net charge which is positive in the difluoroamines, leading to a repulsive polar interaction in perfluoromethylamine (Fig. 5).

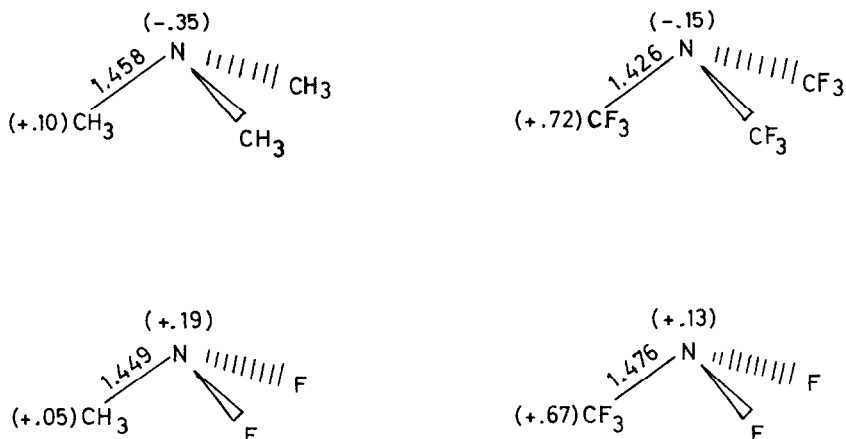


Fig. 5.  $\text{CH}_3/\text{CF}_3$  substitution effect in  $\text{N}(\text{CF}_3)_3$  [8,11] and in  $\text{CF}_3\text{NF}_2$  [12,13].

The second example relates to the dependence of the  $\text{CH}_3/\text{CF}_3$  substitution effect on the oxidation number of the central atom. For sulfides we saw a small increase in the S-C bond lengths. In S(IV) compounds, i.e. for sulfoxides, this effect is much stronger and it is again stronger for S(VI) compounds, the sulfones (Fig. 6). These effects can also be rationalized on the basis of net charges. We expect the positive net charge

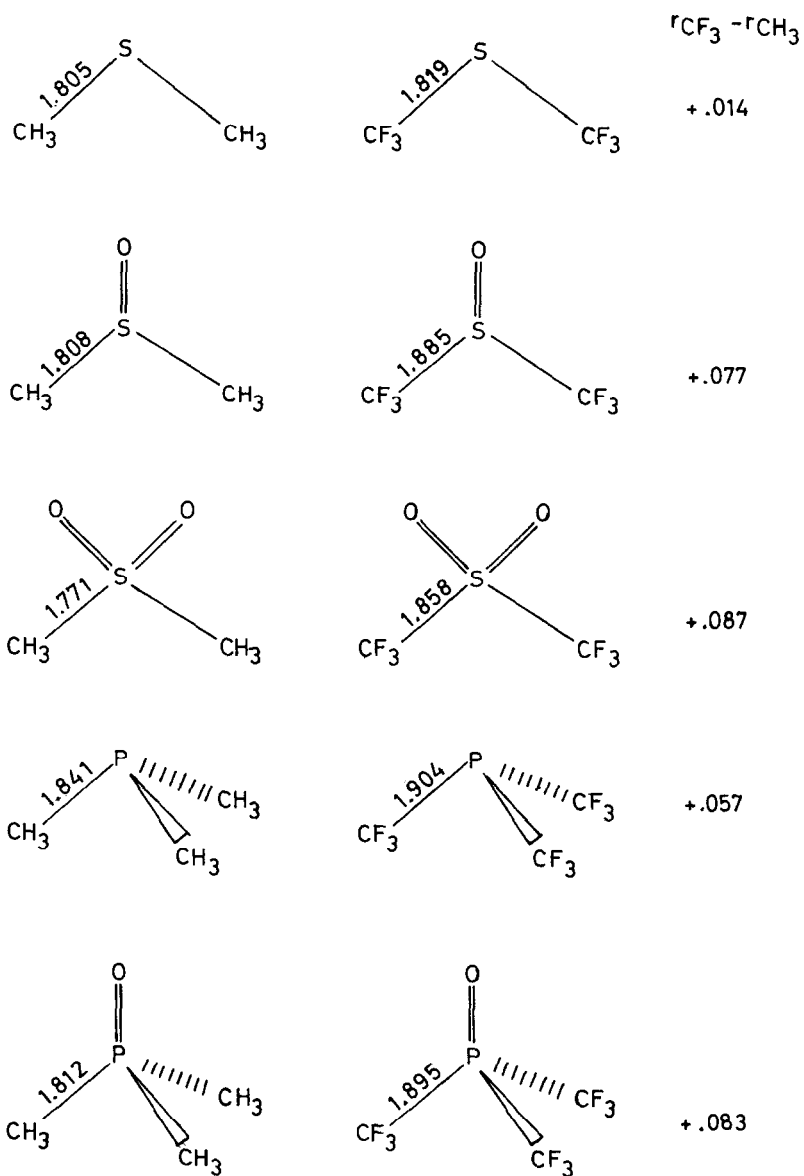


Fig. 6. Dependence of  $\text{CH}_3/\text{CF}_3$  substitution effect and oxidation number [4,5,14-17,8,9,18,19].

of sulfur to increase with increasing oxidation number and consequently the repulsive interactions in the  $\text{CF}_3$  compounds will increase. For the phosphines we had a lengthening of about  $0.06 \text{ \AA}$  and this effect is increased further in the P(V) compounds, i.e. in the phosphine oxides (Fig. 6). Later we will see an even stronger effect for phosphoranes.

#### STERIC EFFECTS OF $\text{CF}_3$ GROUPS

The next aspect of structural effects is the effect of  $\text{CF}_3$  groups on bond angles and we will compare steric requirements of  $\text{CF}_3$  groups with that of fluorine, chlorine and methyl. Starting with the oxygen compounds (Fig. 7) we observe for fluorine

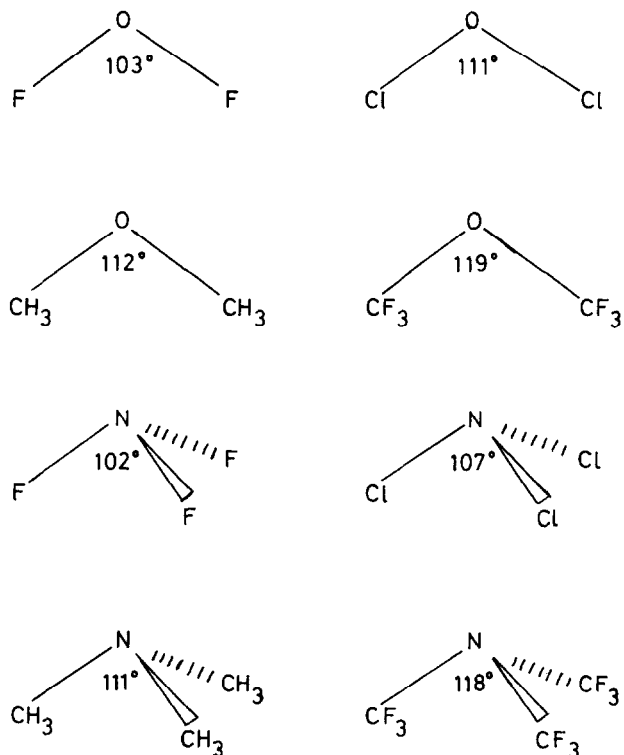


Fig. 7. Bond angles in oxides [21,22,6,7] and amines [23,24,8,11].



and chlorine the well known correlation between bond angles and electronegativity the substituents. This has been rationalized by the rules of the VSEPR model[20] i.e. by repulsions between bonding and/or lone electron pairs. For the methyl compound the trend in the bond angle still agrees quantitatively with this concept. For the  $\text{CF}_3$  compound, however, we observe an increase by about  $7^\circ$  in the oxygen bond angle, although the electronegativity is close to that of chlorine. The very same pattern for bond angles is observed for the amines (Fig. 7), with perfluorotrimethylamine having an almost planar configuration around nitrogen. Both examples, the oxygen and nitrogen compounds, are characterized by short bonds to carbon and direct steric repulsions between  $\text{CF}_3$  groups are important. If the bonds to the  $\text{CF}_3$  groups become longer, such as the C-C bonds in the methane derivatives (Fig. 8), steric repulsions between the  $\text{CF}_3$  groups decrease and their effect on the bond angles becomes less dominant. For even longer bonds, such as in the sulfides (Fig. 9), steric repulsions seem to be negligible and we observe a slight decrease in the sulfur bond angle between the methyl and trifluoromethyl compound, a trend which corresponds to the VSEPR model.

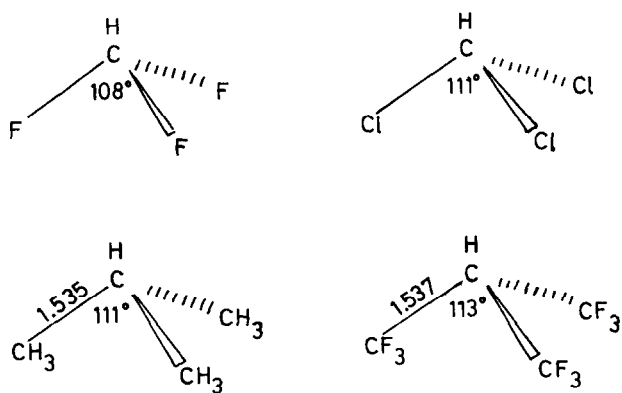


Fig. 8. Bond angles in methane derivatives [25-28].

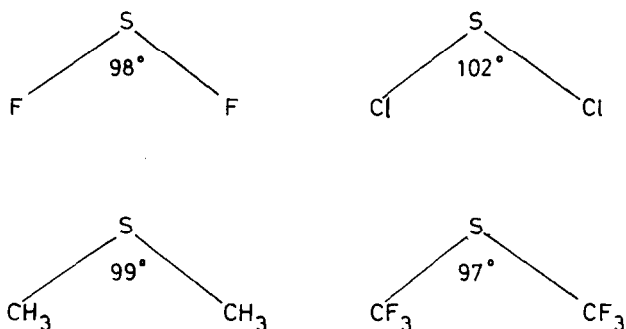


Fig. 9. Bond angles in sulfides [29,30,4,5].

Exactly the same trends in the bond angles are present in the phosphines. Thus, we can summarize these observations in the following way: steric requirements of  $\text{CF}_3$  groups are greater than those of fluorine, chlorine or methyl, if they are bonded to oxygen or nitrogen, i.e. for short bonds, and they are comparable or even smaller than those of their competitors in the case of long bonds, such as in sulfides, phosphines or germanes.

#### $\text{CF}_3$ GROUPS AND STEREOCHEMISTRY OF TRIGONAL BIPYRAMIDAL MOLECULES

According to the VSEPR model the preference for certain ligands for axial or equatorial positions in a trigonal bipyramid depends on their electronegativity: the more electronegative ligands, starting with  $\text{F} > \text{CF}_3 > \text{Cl} > \dots$ , prefer axial positions. For phosphoranes this rule has been slightly modified on the basis of NMR studies, to the Apicophilicity series [31], interchanging the positions of Cl and  $\text{CF}_3$  (i.e.  $\text{F} > \text{CF}_3 > \text{Cl} > \dots$ ). In both cases, however, should fluorine always claim the axial positions against all other competitors.

For trifluoromethyl tetrafluorophosphorane, however, we find controversial results in the literature. In historical order,  $^{19}\text{F}$  NMR spectra [32] were interpreted in terms of axial position of the  $\text{CF}_3$  group and this interpretation was con-

firmed by microwave spectroscopy [33]. On the other hand, i.r. spectra [34] are interpreted in terms of an equatorial  $\text{CF}_3$  group and this result is supported by  $^{13}\text{C}$  NMR data [35]. Semiempirical MO calculations [36] also favour the equatorial conformer by 27 kcal/mole. A similar discrepancy exists for bis(trifluoromethyl) trifluorophosphorane, where  $^{19}\text{F}$  NMR data [32] are interpreted in terms of axial  $\text{CF}_3$  groups, while  $^{13}\text{C}$  NMR data [35] favour the equatorial positions of the  $\text{CF}_3$  groups, in a

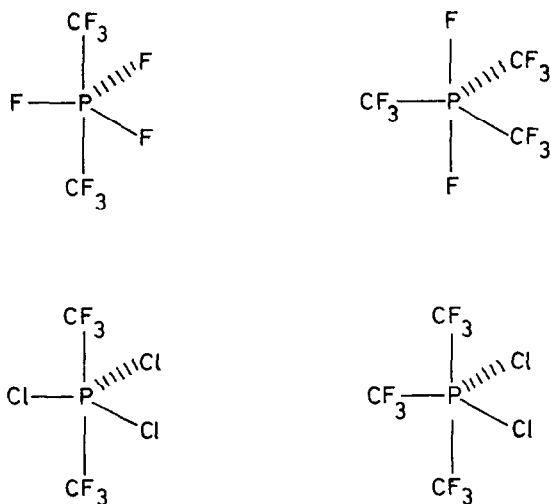
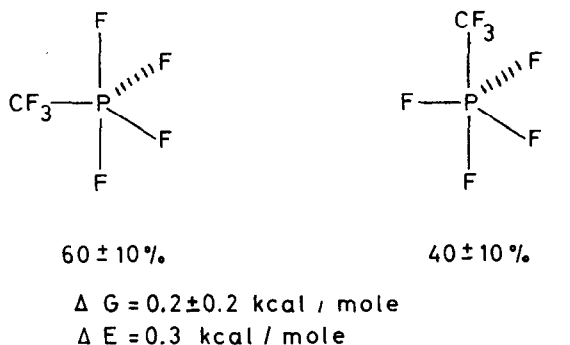


Fig. 10. Stereochemistry of some phosphoranes.

agreement with the two previous rules. The result of the electron diffraction study [37] is kind of a Solomonic decision for  $\text{CF}_3\text{PF}_4$ : the presence of a mixture of both conformers, about 60% equatorial and 40% axial (Fig. 10). This implies a very small difference in the free enthalpies and this is confirmed by ab initio calculations [38] which predict an energy difference of only 0.3 kcal/mole, in strong disagreement with the value obtained from semiempirical calculations. The presence of a mixture of two conformers for this phosphorane is also observed in the matrix i.r. spectra [39].

In the case of  $(\text{CF}_3)_2\text{PF}_3$  the electron diffraction study [37] confirms the interpretation of the  $^{19}\text{F}$  NMR spectra, i.e. two axial  $\text{CF}_3$  groups (Fig. 10). This result contradicts the interpretation of the  $^{13}\text{C}$  NMR spectra and the two empirical rules. Only for  $(\text{CF}_3)_3\text{PF}_2$  all experimental studies -  $^{19}\text{F}$  and  $^{13}\text{C}$  NMR spectra and electron diffraction - come to the same result which is also in agreement with the empirical rules: three equatorial  $\text{CF}_3$  groups (Fig. 10). It is difficult to rationalize the results for these three phosphoranes and we certainly have to consider other effects beside the repulsions between bonding electron pairs.

If  $\text{CF}_3$  groups compete with chlorine atoms for the axial positions in a phosphorane, electron diffraction studies [40] confirm the stereochemistry predicted by the electronegativity rule, i.e. the more electronegative  $\text{CF}_3$  groups prefer the axial positions (Fig. 10). Knowing the stereochemistry of  $(\text{CF}_3)_2\text{PF}_2$ , the result for  $(\text{CF}_3)_2\text{PCl}_2$  is not surprising. It is more difficult to rationalize the difference between  $(\text{CF}_3)_3\text{PF}_2$  and  $(\text{CF}_3)_3\text{PCl}_2$ . It seems, as if the electronegativity effect dominates in the chloro phosphoranes, while additional effects - maybe steric interactions between the  $\text{CF}_3$  groups - are more important for the fluoro phosphoranes.

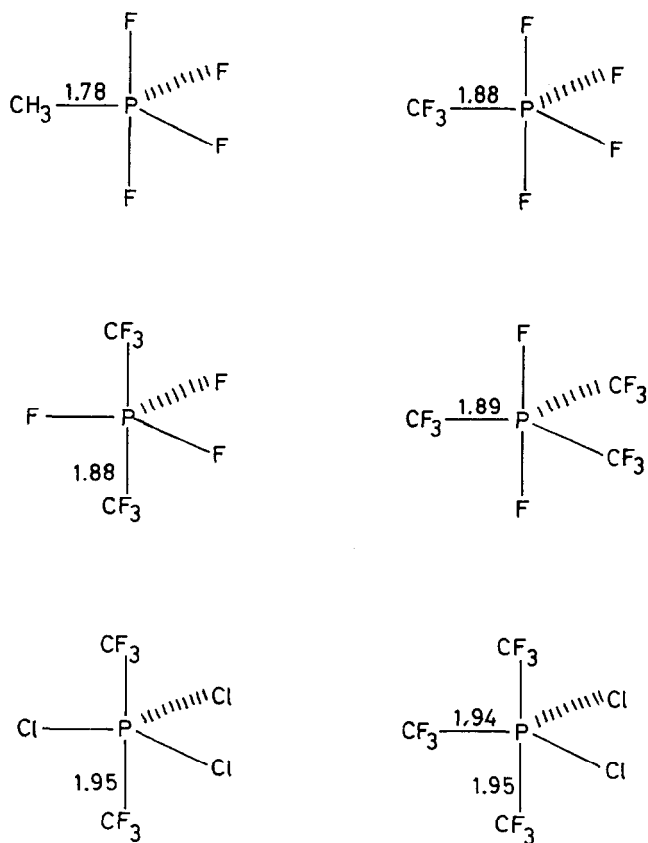


Fig. 11. P-C bond lengths in phosphoranes [ 41,37,40] .

The P-C bond distances in phosphoranes (Fig. 11) show some interesting properties. The effect of  $\text{CH}_3/\text{CF}_3$  substitution - lengthening of  $0.10 \text{ \AA}$  - is larger than any such effect we have seen before. For trigonal bipyramidal molecules we expect axial bonds to be longer than equatorial bonds by 3-8% [42] *i.e.* about  $0.10 \text{ \AA}$  for P-C bonds. Experimentally, however, axial and equatorial P-CF<sub>3</sub> bond lengths in the trifluoromethyl fluoro phosphoranes are almost equal (Fig. 11). In the chloro phosphoranes the P-CF<sub>3</sub> bonds are still longer than in the fluoro phosphoranes and axial and equatorial bond lengths are again equal within the experimental error limits.

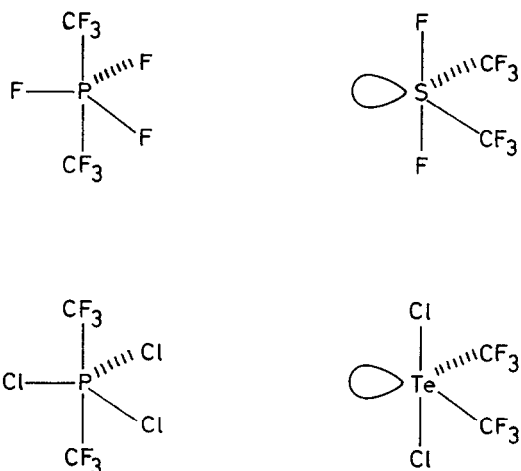


Fig. 12. Stereochemistry of two trigonal bipyramidal molecules with lone electron pairs.

The situation concerning the stereochemistry of trigonal bipyramidal molecules becomes even more confusing, if we add two examples with lone electron pairs on the central atom (Fig. 12). In  $(\text{CF}_3)_2\text{SF}_2$  [15] the  $\text{CF}_3$  groups occupy equatorial positions, in perfect agreement with the two rules. Thus, the formal replacement of an equatorial single bond in the analogous phosphorane by a lone pair changes the stereochemistry. Unfortunately, the S(IV) compound analogous to  $(\text{CF}_3)_2\text{PCl}_3$  is not known, but in the corresponding tellurium compound [43] the stereochemistry is also changed by the presence of a lone pair. Summarizing these observations we see that the stereochemistry of trigonal bipyramidal molecules containing F, Cl and  $\text{CF}_3$  groups seems to be the result of a very delicate balance of several effects and we certainly need more experimental data until we can rationalize these results on the basis of a simple concept.

## REFERENCES

- 1 V. Typke, M. Dakkouri and H. Oberhammer, *J. Mol. Struct.* 44 (1978) 85
- 2 G.K. Pandey and H. Dreizler, *Z. Naturforsch.* 32a (1977) 482
- 3 C.J. Marsden and G.M. Sheldrick, *J. Mol. Struct.* 10 (1971) 405
- 4 T. Iijima, S. Tsuchiya and M. Kimura, *Bull. Chem. Soc. Japan*, 50 (1977) 2564
- 5 H. Oberhammer, W. Gombler and H. Willner, *J. Mol. Struct.* 70 (1981) 273
- 6 K. Kimura and M. Kubo, *J. Chem. Phys.* 30 (1959) 151
- 7 A. H. Lowrey, C. George, P. D'Antonio and J. Karle, *J. Mol. Struct.* 63 (1980) 243
- 8 B. Beagley and A.R. Medwid, *J. Mol. Struct.* 38 (1977) 229
- 9 C.J. Marsden and L.S. Bartell, *Inorg. Chem.* 15 (1976) 2713
- 10 H. Oberhammer, *J. Mol. Struct.* 28 (1975) 349
- 11 H. Bürger, H. Niepel, G. Pawelke and H. Oberhammer, *J. Mol. Struct.* 54 (1979) 159
- 12 L. Pierce, R.G. Hayes and J.F. Beacher, *J. Chem. Phys.* 46 (1967) 4352
- 13 H. Oberhammer, H. Günther, H. Bürger, F. Heyder and G. Pawelke, *J. Phys. Chem.* 86 (1982) 664
- 14 V. Typke, *Z. Naturforsch.* 33a (1978) 842
- 15 H. Oberhammer, R.C. Kumar, G.D. Knerr and J.M. Shreeve, *Inorg. Chem.* 20 (1981) 3871
- 16 M. Hargittai and I. Hargittai, *J. Mol. Struct.* 20 (1974) 283
- 17 H. Oberhammer, G.D. Knerr and J.M. Shreeve, *J. Mol. Struct.* 82 (1982) 143
- 18 C.J. Wilkins, K. Hagen, L. Hedberg, Q. Shen and K. Hedberg, *J. Am. Chem. Soc.* 97 (1975) 6352
- 19 C.J. Marsden, 9th Austin Symposium on Molecular Structure, Austin, Texas, 1982
- 20 R.J. Gillespie, *Angew. Chem. Internat. Edit.* 6 (1967) 819
- 21 Y. Morino and S. Saito, *J. Mol. Spectr.* 19 (1966) 435
- 22 N. Nakata, M. Sugie, H. Takeo, C. Matsumura, T. Fukuyama and K. Kuchitsu, *J. Mol. Spectr.* 86 (1981) 241
- 23 M. Otake, C. Matsumura and Y. Morino, *J. Mol. Spectr.* 28 (1968) 316

- 24 G. Gazzoli, P.G. Favero and A. Del Borgo, J. Mol. Spectr. 50 (1974) 82
- 25 S.N. Gosh, R. Tambarulo and W. Gordy, J. Chem. Phys. 20 (1952) 605
- 26 M. Jen and D.R. Lide, J. Chem. Phys. 36 (1962) 2525
- 27 R. L. Hilderbrandt and J.D. Wieser, J. Mol. Struct. 15 (1973) 27
- 28 R. Stolevick and E. Thom, Acta Chem. Scand. 25 (1971) 3205
- 29 D.R. Johnson and F.X. Powell, Science 164 (1969) 950
- 30 Y. Morino, Y. Murata, Z. Ito and J. Nakamuro, J. Phys. Soc. Japan 17 B-II (1962) 37
- 31 R.G. Cavell, D.D. Poulin, K.I. The and A.J. Tomlinson, J. Chem.Soc. Chem. Comm. (1974) 19
- 32 E.L. Muetterties, W. Mahler and R. Schmutzler, Inorg. Chem. 2 (1963) 613
- 33 E.A. Cohen and D.C. Cornwell, Inorg. Chem. 7 (1968) 398
- 34 J.E. Griffiths, J. Chem. Phys. 49 (1968) 1307
- 35 R.G. Cavell, J.A. Gibson and K.I. The, J. Am. Chem. Soc. 99 (1977) 7841
- 36 P. Gillespie, P. Hoffman, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, E.A. Tsolis and I. Ugi, Angew. Chem. 83 (1971) 691
- 37 H. Oberhammer, J. Grobe and D. Le Van, Inorg. Chem. 21 (1982) 275
- 38 M. v. Carlowitz, J.E. Boggs and H. Oberhammer, unpublished
- 39 H. Willner, unpublished
- 40 H. Oberhammer and J. Grobe, Z. Naturforsch. 30b (1975) 506
- 41 L.S. Bartell and K.W. Hansen, Inorg. Chem. 4 (1965) 1775
- 42 R.J. Gillespie, Molecular Geometry, Van Nostrand Reinhold, London, 1972
- 43 K. Ramme, H. Oberhammer and D. Naumann, unpublished