Journal of Fluorine Chemistry, 19 (1982) 349–362
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PHOTOELECTRON SPECTRA OF GROUP V COMPOUNDS. IX [1]. THE RELATIVE PERFLUOROALKYL SUBSTITUENT EFFECT

S. ELBEL,* H. TOM DIECK

Institut für Anorganische und Angewandte Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-2000 Hamburg 13 (F.R.G.)

and R. DEMUTH

Eduard-Zintl-Institut der Technischen Hochschule Darmstadt, Hochschulstr. 4, D-6100 Darmstadt (F.R.G.)

SUMMARY

The gas phase He I p.e. spectra of the series $(CF_3)_3E$ (E = N, P, As, Sb) and $(CF_3)_nAsH_{3-n}$ are discussed and compared to those of their methylated analogs. The perfluoroalkyl effect - synonymous with large σ-electron withdrawal - causes a nearly parallel stabilization of all m.o. energies as compared with the respective alkyl counterparts. This property can be used, systematically and generally, as a valuable aid for a more precise interpretation of the p.e. spectra of the parent methyl derivatives. Band superposition due to interfering substituent m.o. energies is diminished without destroying the original orbital energy sequence found for the methyl compounds. Overlapping bands from the ionisation of σ- and π-type skeletal molecular orbitals can be resolved on replacing alkyl by perfluoroalkyl groups. Substituent effects including R = CF_3, Hal, SiR'_3 and H are surveyed for the series ER_3 (E = N, P).

INTRODUCTION

He I gas phase photoelectron spectrometry (p.e.s.) is usually regarded as dealing with binding energies of valence electrons occuring between ca. 7 to 21 eV. Due to losses of intensity and resolution with increasing ionisation potentials the wealth of spectral information decays above 16 - 17 eV. High energy bands are often neglected or are only tentatively assigned. The majority of substances investigated with p.e.s. so far has been organic compounds containing many C–H bonds. Here, the p.e. energy region is further decreased to the small gap between 7 - 12 eV because bands at higher energies are often obscured beneath broad and unstructured C–H "mountains". For many types of compounds (cf. amines, ethers, ketones, alcohols, etc.) the information sometimes consists of a single ionisation potential (i.p.). We will show how information that is lost under C–H band complexes can be regained or even enlarged upon replacing alkyl by perfluoroalkyl groups and how the utilization of substituent effects in general can contribute to a more precise assignment of the p.e. spectra of analogous compounds using a series of perfluoroalkyl derivatives of group V elements.

EXPERIMENTAL

The alkylamines were purchased from Fluka AG, CH-Buchs. Perfluoro-tri-n-butylamine was a gift of the Hoechst AG, D-Frankfurt/M-Hoechst. All other compounds were prepared by literature procedures. The 584 Å p.e. spectra were recorded on a Perkin Elmer PS 16 spectrometer and were calibrated with argon and xenon. The estimated error in the i.p.s. is ± 30-40 meV. The resolution ranged between 25-40 meV. - CNDO/2 and Extended Hückel m.o. calculations were performed using the Univac 1108 computer of the University of Frankfurt/M.

RESULTS AND DISCUSSION

The definition of the perfluoroalkyl substituent effect

The perfluoroalkyl substituent effect with the CF_3 prototype is well documented [2-4]. CF_3 is usually thought to be a relatively pure electron withdrawer (dominant -I-effect) stabilizing both σ and π energies when compared to the corresponding methyl species.

P.e. spectra of CF_3 substituted group V compounds have been presented primarily by Cowley et al. [5] and by us [6], but they were rarely used to help in the interpretation of the p.e. spectra of the parent CH compounds [6,7].

To illustrate impressively the different effects of alkyl and parent perfluoroalkyl substituents the p.e. spectra of the amines $(n\text{-}C_4H_9)_3N$ (1) and $(n\text{-}C_4F_9)_3N$ (2) are shown in figure 1:

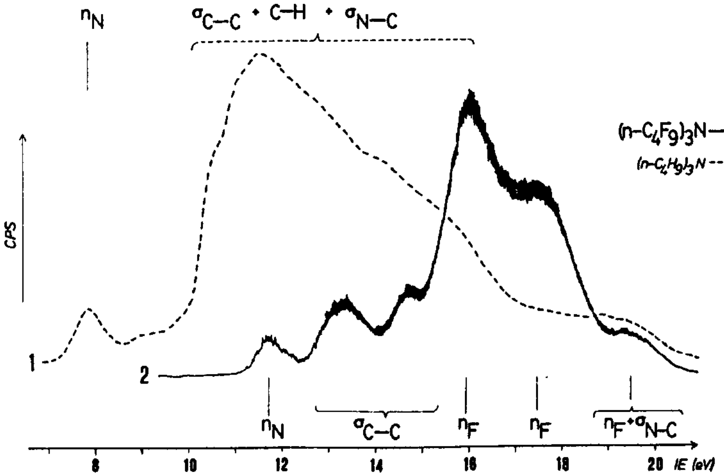

Fig. 1. The He I p.e. spectra of the amines $(n\text{-}C_4H_9)_3N$ (1) (dashed line) and $(n\text{-}C_4F_9)_3N$ (2)(full line) assigned qualitatively.

In 2 fluorine lone pair molecular orbital i.p.s., n_F, and the bonding m.o. ionisation potentials, σ_{C-F}, occur in the high energy region of the spectrum revealing two more bands in the σ_{C-C} range with respect to 1. Assuming a similar band shift for n_N and σ_{N-C} bands - reflecting the trend for n and σ bands of representative phosphines [6] - on going from 1 to 2, these two new bands in 2 should be located near the low energy edge of the C–H band in 1. With the further assumption that 1 and 2 have similar conformations the energy level sequence and the m.o. type of the σ_{C-C} m.o.s. should be the same in both compounds. This is our definition of the "perfluoroalkyl effect" in u.v. p.e.s.: With respect to parent alkyl groups C_nF_{2n+1} substituents exert a quasi parallel stabilization of central atom (n) and σ m.o.s. without changing their sequence, energy difference and m.o. type.

The substituent i.p.s. n_F and σ_{C-F} in figure 1 show more structure as compared with the C–H i.p.s. of 1. This is characteristic for all compounds bearing perfluoroalkyl substituents and is already established from the n_F/σ_{C-F} pattern in HCF_3 [8] (see also below). The vertical i.p.s. and band maxima of all p.e. spectra presented here are summarized in the table.

The series $(CF_3)_3E$ and Me_3E

The photoelectron spectra of Me_3E (E = N, P, As, Sb) [9] and of $(CF_3)_3N$ [10], $(CF_3)_3P$ [5a], $(CF_3)_3As$ and $(CF_3)_3Sb$ are depicted in figure 2.

Previous interest in Me_3E was mainly with the relative energies of their lone pair m.o.s. which show nearly constant ionisation potentials [9]. Compared to the attention paid to these first ionisation energies (IE_1) of Me_3E the most obvious band corresponding to the bonding m.o. i.p.s. σ_{E-C} (degenerate in C_{3v}) seemed to be ignored. Their assignment is straightforward for E = P, As, Sb in both series, where they are attributed to the second bands in each spectrum [9]. For trimethylamine (3) three possible assignments have been reported so far: The degenerate σ_{N-C} energy has to be localized

(i) in the third band at 15.7 eV [11];
(ii) at the low energy side within the C–H band [12];
(iii) inside the C–H band as in (ii) and in the third band as in (i) since strong interaction of σ_{N-C} with C–H m.o.s. of appropriate symmetry (e) and nearby energy could give rise to two bands, designated σ_{N-C-H} [9].

TABLE

Vertical ionisation potentials and p.e. band maxima of perfluoroalkyl and alkyl analogs of group V elements and of parent compounds.

1	$(n\text{-}C_4H_9)_3N$	7.86, 10.3 - 16.0^a (11.55^b)
2	$(n\text{-}C_4F_9)_3N$	11.70, 13.33, 14.75, ca. 17.5, 19.35
3	$(CH_3)_3N$	8.54, 11.8 - 14.4^a (12.83^b, 13.73^b), 15.70, 19.4
4	$(CF_3)_3N$	12.55, 15.3 - 17.2^a (15.95^b), 17.8, 19.3
5	$(CH_3)_3P$	8.60, 11.35, 12.8 - 15.7^a (13.7^b, 14.7^b), 19.6
6	$(CF_3)_3P$	11.57, 13.44, 15.8^b, 17.25
7	$(CH_3)_3As$	8.65, 10.70, 12.6 - 15.3^a (13.55^b)
8	$(CF_3)_3As$	11.41, 12.77, 15.7^b, 17.1, ca. 19.8
9	$(CH_3)_3Sb$	8.48, $\overline{10.3}$, 12.4 - 14.7^a (13.3^b)
10	$(CF_3)_3Sb$	10.74, 11.97, 15.42^b, 17.0, 20.26^b
11	AsH_3 [16]	10.58, $\overline{12.7}$
12	CH_3AsH_2	9.50, 11.2 - 12.6^a (11.65^b, 12.02^b), 13.5 - 15.2^a
13	CF_3AsH_2	11.00, 12.73, 13.39, 15.0, 15.6, 16.7, 18.0
14	$(CH_3)_2AsH$	8.87, 10.5 - 11.9^a (11.35), 12.85 - 15.30^a
15	$(CF_3)_2AsH$	11.26, $\overline{12.63}$, 13.31, 15.45^b, 17.0
16	CH_3NH_2	9.65, 13.2, 14.3, 15.3, 16.7, 21.8
17	CH_3PH_2	9.62, 11.8 - 13.3^a (12.27^b), 13.9 - 15.7^a
18	CF_3PH_2	11.15, 13.3, 14.12, 15.08, 15.82, 16.83, 18.15
19	HCF_3 [8]	14.80, 15.50, 16.16, 17.24, 20.8

a) halfwidth of the band complex. b) maximum of the band complex

Substitution of Me by CF_3 should clarify this problem: If the σ_{N-C} ionisation potential is regarded as to be covered by the low energy C–H bands (ca. 11.5 - 12.5 eV, fig. 2; assignment ii) it should emerge on 'shifting' the substituent m.o. energies to higher i.p.s. with CF_3 groups. But, there is obviously no new band between n_N and n_F in the p.e. spectrum of $N(CF_3)_3$ (4) (figure 2). Hence, the σ_{N-C} i.p. in Me_3N should be correspondingly assigned to the third band at 15.7 eV. If the

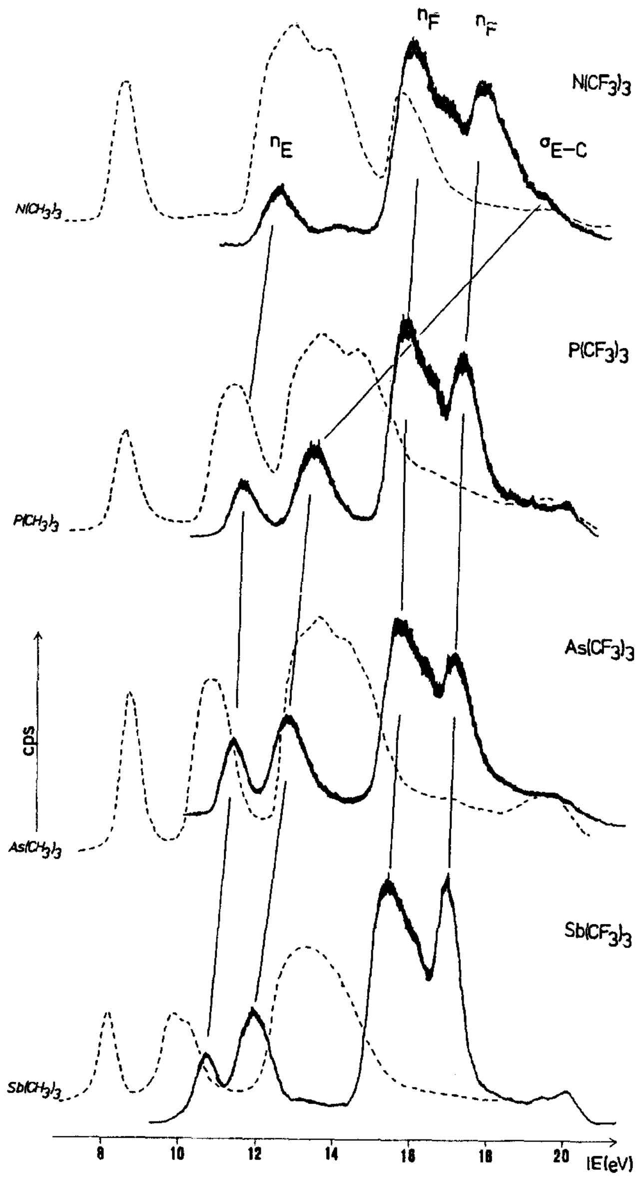

Fig. 2. The He I p.e. spectra of the series $(CF_3)_3E$ and Me_3E (E = N, P, As, Sb) with qualitative assignment for $(CF_3)_3E$ (full lines).

lone pair i.p. shift Δn_N ($\underline{3} \longrightarrow \underline{4}$) of ca. 4 eV is taken as a measure for the overall stabilization of the NC_3 skeletal m.o. energies, the σ_{N-C} (e) band in $\underline{4}$ should occur in the high energy range and is assigned to the high energy shoulder of the n_F band at ca. 19.35 eV ($\Delta\sigma_{N-C}$ = 3.6 eV).

Observing the relative positions of n_F/σ_{C-F} and σ_{E-C} bands in $(CF_3)_3E$ there is a crossover of the respective correlation lines between the amine and the phosphine. This is true for the series Me_3E and is a common feature in all cases where the p.e. spectra of second row compounds are compared to those of the heavier homologs (i.e. E = P, As, Sb) [13,6b]. This peculiarity is caused by stronger interaction between the nitrogen atomic orbitals (a.o.s.) and appropriate substituent orbitals which show a reversed energy sequence as compared with the corresponding phosphorus (or As, or Sb) a.o.s. or appropriate fragment m.o.s. In figure 3a the m.o. models based on the 'composite molecule' m.o. approach and the p.e. spectral assignments for the model series $MeNH_2$ [12,14] ($\underline{16}$), $MePH_2$ [15,6a] ($\underline{17}$) and $MeAsH_2$ ($\underline{12}$) are illustrated. Here, the reason for the interconversion (marked by the arrow) of the correlation lines can be traced back distinctly.

The lone pair orbital energies n_E for $(CF_3)_3E$ are easily assigned to the first bands for each compound. They show the expected small change due to the opposite effects of E sp^x hybridization and E valence shell ionisation potentials, on going from N to Sb, as also found for n_{EH_3} [9,16]. A constant functional interdependence between n_E and E as is observed for Me_3E[9] is not expected here where hyperconjugative effects are disregarded in the first order. Nevertheless, the small change ΔIE_1 between $N(CF_3)_3$ [10] ($\underline{4}$) and $P(CF_3)_3$ [5a] ($\underline{6}$) is not as pronounced as might be expected on the basis of the E_p v.s.i.p.s. This may be rationalized by the nearly planar skeleton of $\underline{4}$ (∢ CNC = 114°) [18] as compared to $\underline{3}$ (∢ CNC = 110.6°) [19] giving a quasi pure 'p-type' n_N lone pair m.o. for $\underline{4}$.

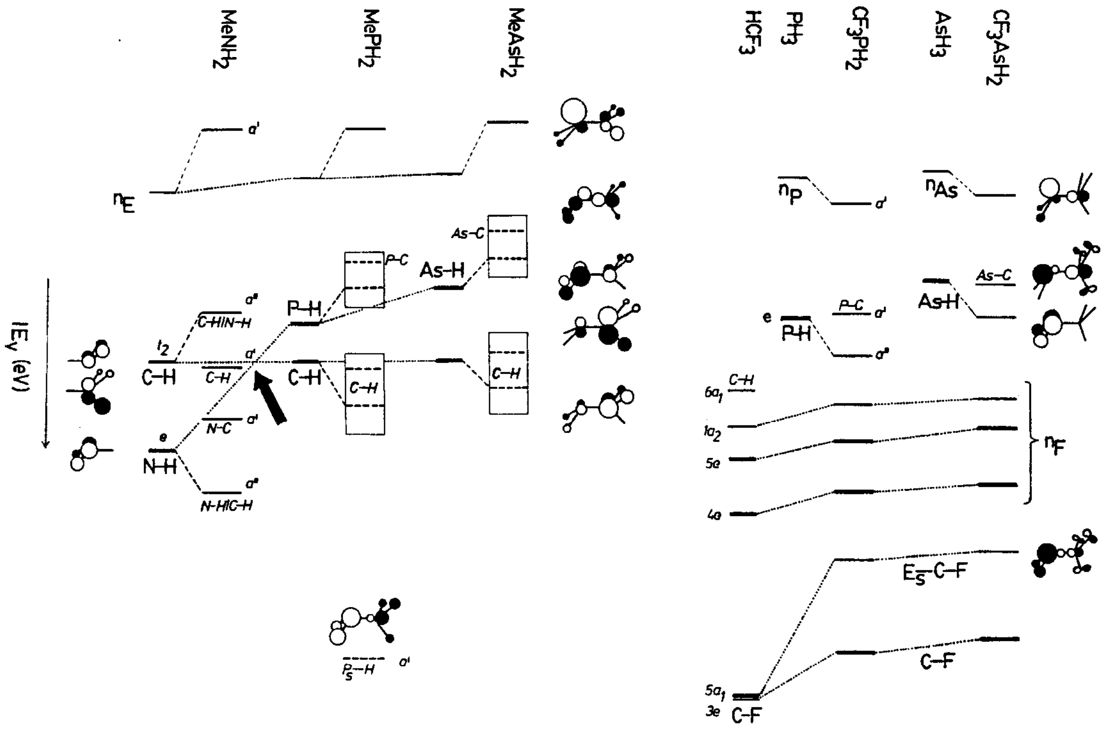

Fig.3. a) He I p.e. data of the series MeNH$_2$ (E = N, P, As) as assigned by a 'composite molecule' m.o. approach based on the p.e. data of EH$_3$ [16] and CH$_4$ [17]; the interconversion of σ_{E-C}/C–H i.p.s. is marked by an arrow.

b) He I p.e. data of CF$_3$PH$_2$ [5a] and CF$_3$AsH$_2$ correlated with HCF$_3$ i.p.s. [8] and illustrated by EHMO - eigenfunctions for CF$_3$PH$_2$.

The series $(CF_3)_nAsH_{3-n}/Me_nAsH_{3-n}$ (n = 0, 1, 2, 3)

The He I p.e. spectra of both series are presented in figure 4. As is clearly seen, the lone pair i.p.s. (IE_1) are successively stabilized upon introducing the CF_3 groups. This is consistent with their dominant (-)I-effect and is in contrast to the destabilizing effect of methyl groups where a (+)I-effect and appreciable hyperconjugation are present.

With respect to the order of the $|e_{As-C}|(\underline{8}) < |e_{As-H}|(\underline{11})$ [16] energies, the second bands of both C_s members $\underline{13}$ and $\underline{15}$ are assigned to m.o.s. exhibiting predominant σ_{As-C} bonding character. The third bands are attributed to ionisations from typical As–H m.o.s. following the correlation lines for the CF_3 substituted arsines in fig. 4. Since the bands are best resolved for CF_3AsH_2 this will be used as model compound for the discussion of the whole As series and of CF_3 derivatives of the other group V elements. The arguments given below follow the illustrations in figure 3b where the m.o. types and energies of CF_3EH_2 (E = P [5a], As) are derived from HCF_3 [8] and EH_3 [16].

n_F/σ_{C-F} bands: These show a slight high energy shift with increasing number of CF_3 groups. Their splitting pattern as well as the band contours persist throughout the series presented in figs. 1 and 4. They correspond very well to the n_F and σ_{C-F} energies of HCF_3 suggesting that local C_{3v} symmetry of the CF_3 fragment is retained in C_s. Under this assumption the typical n_F m.o.s. of the CF_3 substituent that are not involved in σ-type bonding transform as 1 x a_2 and 2 x e. a_1 m.o.s. mix into σ_{C-F} and σ_{As-C} bonding m.o.s. and are therefore neglected.

The n_F m.o.s. are distributed as follows:

15.5 - 16 eV n_F orbitals of local a_2 symmetry followed by degenerate m.o.s. that exhibit some central atom antibonding character. The local a_2 m.o. of CF_3 shows no contribution from the centre C because of its unique symmetry. Provided geometry changes depending on R in RCF_3 are negligible, these can be used to determine the relative (σ) inductive effect of R in general.

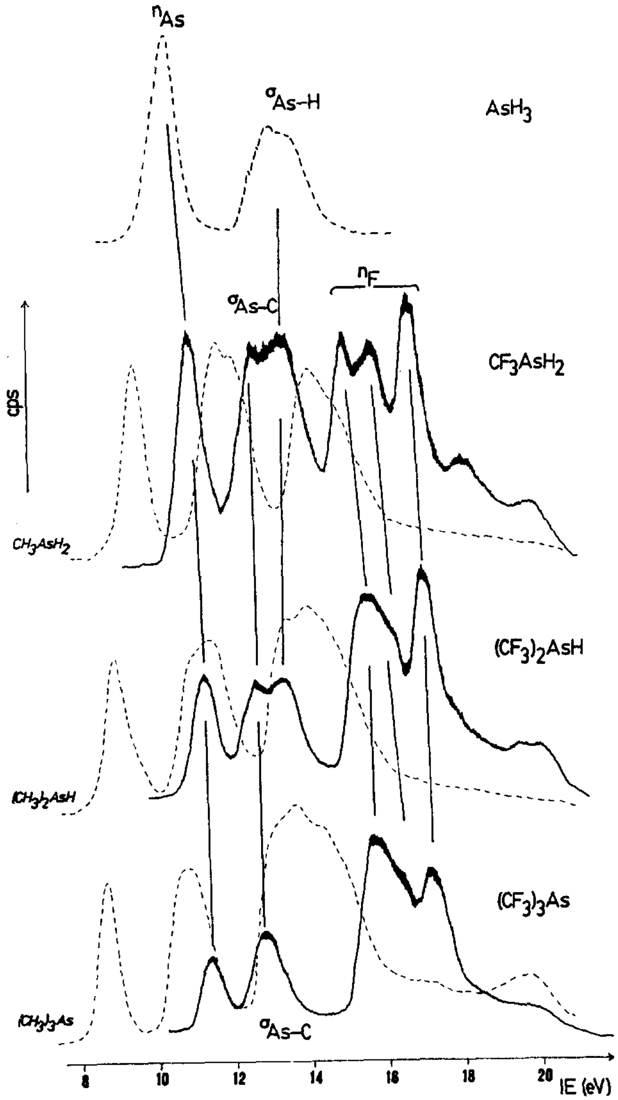

Fig.4. The He I p.e. spectra of the series $(CF_3)_nAsH_{3-n}$ (full line) and Me_nAsH_{3-n} (dashed line).

The qualitative assignment refers to the CF_3 arsines.

16.8 - 17.3 eV purely nonbonding m.o.s. of e symmetry.

Since replacement by the strongly electron withdrawing CF_3 groups will increase the effective nuclear charge of E, the skeletal $C—EH_2$ m.o.s. (which correspond to the 5a', 4a' and 2a'' m.o.s. in $MeEH_2$) are stabilized. In contrast, n_F and $\sigma_{C—F}$ m.o.s. are destabilized relative to HCF_3 [8] on formation of CF_3EH_2. The smaller the group electronegativity for R in RCF_3, the greater the upward shift of the characteristic CF_3 m.o.s. towards that of the CF_3^- anion (figure 3b).

P.e. bands lacking correlation with original CF_3 bands are assigned to orbitals having appreciable electronic charge density in the $C—EH_2$ trunk. For this reason the $5a_1$ m.o. in HCF_3 (20.8 eV) [8] corresponds to the 18.0. eV band in CF_3AsH_2. It can be ascribed to a H—As—C(F) type m.o. (see m.o. diagrams from semiempirical calculations in fig. 3b).

The hyperconjugative model for $MeEH_2$ as depicted in figure 3a is no longer valid for CF_3EH_2. Both σ- and π-type orbitals will be stabilized upon replacement of CH_3 by CF_3 in any compound. This is true for n_E (a'), $\sigma_{E—H}$ (a'') and $\sigma_{E—C}$ (a') m.o.s. with respect to $MeEH_2$ and EH_3 [16] (figure 3b). However, as can be seen from the table and figs. 3b and 4, the lowering in energies of the orbitals of pseudo-π-symmetry, i.e. $\sigma_{E—H}$ and partially n_E, is less pronounced relative to $\sigma_{E—C}$. This fact indicates only a small hyperconjugative contribution to the total CF_3 substituent effect. The difference is however large enough to separate the components of the second bands which strongly overlap in the alkyl derivatives. The CF_3 substituent effect shows yet a further useful property: It can be applied as a diagnostic tool for the discrimination of the i.p.s. of σ- and π-type m.o.s. which cannot be interpreted in the methyl compounds due to superposition. In this respect CF_3 groups are similar to the effects of oxidizing ER_3 with acceptors X to form R_3EX (X = O, S, etc.). The overall stabilization of the i.p.s. of the original R_3E frame can be differentiated according to the m.o. type: Orbitals possessing σ-bonding contributions are affected more than levels of π-type representations [20].

C_nF_{2n+1} within the scale of substituent effects - an appreciation

To date, perfluoroalkyl compounds have not received much attention in photoelectron spectroscopy. This is partly because of preparative difficulties, although the perfluoroalkyl substituent effect appears partly to be of "secondary importance" with respect to the popular alkyl or the special "perfluoro" effect [21]. Perfluoroalkyl groups are usually considered to be purely electron withdrawing and lacking in differentiation. We have shown that the predominant σ-electron withdrawal which is partially balanced by π-donation allows important and new analytical interpretation of the p.e. data of their alkyl analogs. Replacing alkyl by perfluoroalkyl can help to clear relevant sections of the spectra since the interfering substituent i.p.s. are removed to higher energies. Further, bands due to ionisations from σ- and π-type m.o.s. are often separated. - CF_3 is not as strong an electron acceptor as

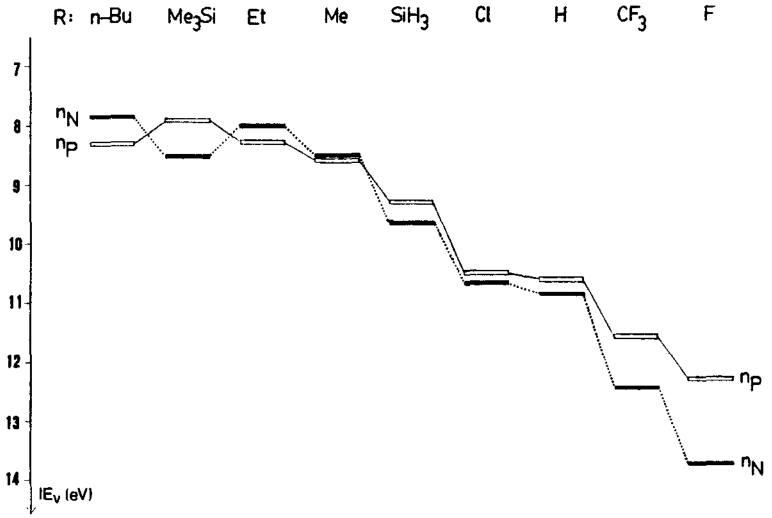

Fig.5. The scale of the relative overall substituent effects as represented by the first i.p.s. (n_E) of tertiary amines (full bars) and phosphines (empty bars), ER_3.

fluorine, but is next to it in electronegativity [cf. 6b]. This is shown indirectly by the trend of the n_E i.p.s. of representative group V compounds in figure 5.

REFERENCES

1 Part VIII: S. Elbel and H. tom Dieck, Z. anorg. allg. Chem., (1981); accepted for publication.

2 C.J. Marsden and L.S. Bartell, Inorg. Chem., 15 (1976) 2713.

3 H. Oberhammer, J. Mol. Struct., 28 (1975) 349.

4 A. Greenberg, J.F. Liebman and D. van Vechten, Tetrahedron, 36 (1980) 1161; W.A. Sheppard, J. Amer. Chem. Soc.,87 (1965) 2410; D. Holtz, Chem. Rev., 71 (1971) 139; J.F.A. Williams, Tetrahedron, 18 (1962) 1477; J.D. Hepworth, J.A. Hudson, D. A. Ibbitson and G. Hallas, J.C.S. Perkin II, (1972) 1905; M. N. Paddon-Row, C. Santiago and K.N. Houk, J. Amer. Chem. Soc., 102 (1980) 6561.

5 a) A.H. Cowley, M.J.S. Dewar and D.W. Goodman, J. Amer. Chem. Soc., 97 (1975) 3653; b) A.H. Cowley, M.J.S. Dewar, M. Lattmann, J.L. Mills and M. McKee, Ibid., 100 (1978) 3349.

6 a) S. Elbel, H. tom Dieck and R. Demuth, Z. Naturforsch., 31b (1976) 1472; b) S. Elbel and H. tom Dieck, Ibid., 31b (1976) 178.

7 H. Bergmann, S. Elbel and R. Demuth, J.C.S. Dalton, (1977) 401; D.L. Lichtenberger and R.F. Fenske, Inorg. Chem., 13 (1974) 486.

8 e.g. C.R. Brundle, M.B. Robin and H. Basch, J. Chem. Phys., 53 (1970) 2196; W.R. Harshbarger, M.B. Robin and E.N. Lassettre, J. Electron Spectrosc., 1 (1972/73) 328, and literature cited therein.

9 S. Elbel, H. Bergmann and W. Enßlin, J.C.S. Faraday II, 70 (1974) 555.

10 A copy of the He I p.e. spectrum of $N(CF_3)_3$ was kindly given to us by Prof. H. Bürger (Wuppertal) prior to publication.

11 V.I. Vovna and F.I. Vilesov, Opt. Spectrosc., 36 (1974) 251.

12 K. Kimura and K. Osafune, Mol. Phys., 29 (1975) 1073.

13 S. Elbel, H. tom Dieck, H. Walther and J. Krizek, Inorg. Chim. Acta, 53 (1981) L 101.

14 S. Katsumata, T. Iwai and K. Kimura, Bull. Chem. Soc. Japan, 46 (1973) 3391, and literature cited therein.

15 S. Cradock, E.A.V. Ebsworth, W.J. Savage and R.A. Whiteford, J.C.S. Faraday II, 68 (1972) 934.

16 A.W. Potts and W.C. Price, Proc. Roy. Soc., A 326 (1972) 181.

17 e.g. D.W. Turner, C. Baker, A.D. Baker and C.R. Brundle, Molecular Photoelectron Spectroscopy, Wiley-Interscience, London 1970.

18 R.L. Livingston and G. Vaughan, J. Amer. Chem. Soc., 78, (1956) 4866.

19 B. Beagley and T.G. Hewitt, Trans. Faraday Soc., 64 (1968) 2561.

20 S. Elbel and H. tom Dieck, J.C.S. Dalton, (1976) 1762.

21 C.R. Brundle, M.B. Robin, N.A. Kuebler and H. Basch, J. Amer. Chem. Soc., 94 (1972) 1451; M.B. Robin, N.A. Kuebler and C.R. Brundle, Report of the International Conference on Electron Spectroscopy, Asilomar 1971.