Photoelectron Spectra and Bonding of (*N*–*B*)-2,8,9-Trioxa-5-aza-1-bora-bicyclo[3.3.3]undecane (Boratran) and some 2,8,9-Trioxa-5-aza-1-sila-bicyclo[3.3.3]undecanes (Silatrans)

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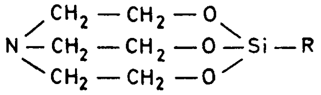
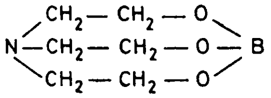
The He(I) photoelectron spectra of silatrans $[N(CH_2CH_2O)_3]SiR$, (I; R = H, Me, or OEt), and boratran $[N(CH_2CH_2O)_3]B$, (II), are compared with those of the non-cage triethoxy-compounds and with that of the parent tris(2-hydroxyethyl)amine. The shifts observed in the N $2p$ lone-pair band are discussed in relation to internal σ-donation to the empty p orbital of boron or d orbitals of silicon and to interaction with oxygen lone-pair levels.

THE silatrans[1] are a class of organic derivatives of silicon of general formula (I). They have interesting structures[2] in which the silicon–nitrogen transannular distance is very short, and other unusual properties[1] including abnormally low basicities and, in some cases, biological activity. It has been suggested[1,2] that the short Si–N distance is due to ($p \rightarrow d$) σ-bonding, just as the short B–N distance[3] in boratran, (II), is due to ($p \rightarrow p$) σ-bonding between N and B.


(I)


(II)

We have investigated the He(I) photoelectron (p.e.) spectra of boratran and some simple silatrans (I; R = H, Me, or OEt) in relation to those of similar molecules where this transannular interaction is impossible. We hoped to see whether any evidence could be obtained for such donation, which should significantly raise the binding energy of the N $2p$ lone-pair level compared to that found in the parent tris(2-hydroxyethyl)amine (tha), $N(CH_2CH_2OH)_3$.

EXPERIMENTAL

Tris(2-hydroxyethyl)amine (tha), boric acid, trichloro(methyl)silane, tetrachlorosilane, and triethoxysilane were commercial products. The chlorosilanes were converted to the corresponding ethoxysilanes by heating them under reflux with excess of ethanol until evolution of HCl had ceased; excess of alcohol was removed by distillation. Boratran[4] was prepared by heating tha and boric acid together to 100 °C and then removing water gradually by reducing the pressure.† When the theoretical yield of water had been collected the product was melted and allowed to crystallise. A pure sample for p.e. spectroscopy was sublimed from the crude product *in vacuo*. Silatran (I; R = H) was prepared[5] by heating crude boratran and triethoxysilane under reflux in xylene with $AlCl_3$ as a catalyst. The product was filtered off after cooling. The substituted silatrans were prepared[6] by heating tha and the ethoxysilanes under reflux in xylene with KOH as a catalyst. The products crystallised on cooling.

The identities and purity of the compounds prepared were checked using m.p.s and i.r. spectra.[1,4] Mass spectra confirmed the molecular structures of boratran and the silatrans. P.e. spectra were run using He(I) (21·22 eV) excitation on a Perkin-Elmer PS16 spectrometer modified to allow evaporation of samples within the instrument.‡

$$N(CH_2CH_2OH)_3 + B(OH)_3 \xrightarrow{\text{heat}} N(CH_2CH_2O)_3B \quad (1)$$

$$N(CH_2CH_2O)_3B + (EtO)_3SiH \xrightarrow[AlCl_3]{\text{xylene}} [N(CH_2CH_2O)_3]SiH + B(OEt)_3 \quad (2)$$

$$N(CH_2CH_2OH)_3 + (EtO)_3SiR \xrightarrow[KOH]{\text{xylene}} [N(CH_2CH_2O)_3]SiR + 3EtOH \quad (3)$$

TABLE 1

Temperatures required for p.e. spectra

Compound	θ_c/°C
$N(CH_2CH_2OH)_3$	75
$[N(CH_2CH_2O)_3]B$	150
$[N(CH_2CH_2O)_3]SiH$	100
$[N(CH_2CH_2O)_3]SiMe$	40
$[N(CH_2CH_2O)_3]Si(OEt)$	100

The title compounds all evaporated at an adequate rate only on heating. The temperatures used are set out in Table 1. Triethoxyboron and the ethoxysilanes were admitted to the spectrometer from a vacuum line through a stainless-steel needle valve. Observed p.e. spectra are shown in Figures 1 and 2.

DISCUSSION

The point of most interest is the binding energy of the nitrogen lone-pair level in each compound. In the parent tha this gave rise to a band *ca.* 1 eV broad (at half height) centred at *ca.* 8·7 eV, though the onset of ionisation (adiabatic ionisation potential) was below 8 eV [Figure 2(*a*)]. The position and appearance of this band were similar to those for other trialkylamines.[7] A second, stronger, broad band centred at *ca.* 10·7 eV is probably due to oxygen lone-pair levels. Even broader bands above 11·5 eV are ascribed to σ-bonding levels derived from $1p$ orbitals of N, O, and C and H $1s$ orbitals. In striking contrast, the spectra of boratran, (II), silatran, (I; R = H), and ethoxysilatran,

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† Boratran, (II) = (*N*–*B*)-2,8,9-trioxa-5-aza-1-borabicyclo-[3.3.3]undecane; silatran, (I; R = H) = 2,8,9-trioxa-5-aza-1-silabicylo[3.3.3]undecane.

‡ 1 eV ≈ 1·60 × 10^{-19} J.

[1] M. G. Voronkov, *Pure Appl. Chem.*, 1966, **13**, 35.

[2] J. F. Turley and F. P. Boer, *J. Amer. Chem. Soc.*, 1968, **90**, 4026; 1969, **91**, 4129, 4134.

[3] H. Follner, *Monatsh.*, 1973, **104**, 477.

[4] B.P. 973,714/1964 (U.S. Borax and Chemical Corporation) (*Chem. Abs.*, 1965, **62**, 3694).

[5] G. I. Zelcans and M. G. Voronkov, *Khim. geterotsikl. Soedinenii*, 1967, 371 (*Chem. Abs.*, 1967, **67**, 108112).

[6] C. L. Frye, G. E. Vogel, and J. A. Hall, *J. Amer. Chem. Soc.*, 1961, **83**, 996.

[7] S. Cradock, unpublished work.

(I; R = OEt), contained no bands below 9·5 eV, showing that the nitrogen lone pair is indeed considerably more tightly bound in these compounds.

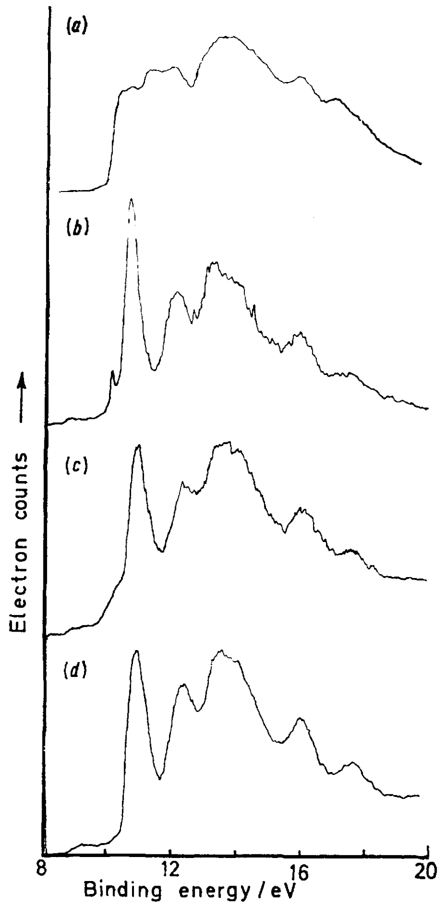

FIGURE 1 He(I) p.e. spectra of: (*a*) $(EtO)_3B$; (*b*) $(EtO)_3SiH$; (*c*) $(EtO)_3SiMe$; (*d*) $(EtO)_4Si$

In methyl silatran, (I; R = Me), there was a band at 8·7 eV; it seems likely that this arises from the N lone-pair level interacting with other levels of comparable energy and the same symmetry. This leads us to consider what interactions of this type may be occurring in this molecule and in the others. Before doing this we must pick out some other salient features of the spectra.

In the spectrum of (II) [Figure 2(*b*)] the two bands at lowest energy were of comparable intensity, the first being rather more intense. They had maxima at 9·8 and 11·1 eV, and were considerably sharper than the bands of tha, with widths at half height of *ca.* 0·7 eV. For (I; R = H) [Figure 2(*c*)] we again found two bands, at 10·4 and 11·2 eV, but there was a shoulder on the former at *ca.* 10·1 eV. For (I; R = Me) [Figure 2(*d*)] two bands appeared in this same region, at 10·2 and 11·0 eV, but a distinct broad band centred at *ca.* 8·7 eV was also present. This is not, apparently, due to tha present as an impurity or produced by hydrolysis of the sample; the stronger band of this compound at 10·7 eV is not compatible with the clear separation of the bands at 10·2 and 11·0 eV. In the spectrum of (I; R = OEt) [Figure 2(*e*)] two bands again occurred, at 10·6 and 11·2 eV. The first was stronger and broader than the second, while a weak broad shoulder near 8·7 eV was also present. In this case it is more likely that this is due to tha produced by hydrolysis, as it was far weaker than the other bands in the spectrum. The compound appears to be readily hydrolysed.

The spectra of the triethoxy-derivatives $(EtO)_3B$, $(EtO)_3SiH$, $(EtO)_3SiMe$ and $(EtO)_4Si$ are shown in Figure 1. The boron compound, which presumably has a planar O_3B skeleton, showed no discrete bands but several overlapping peaks were present between 10 and 12·5 eV. The triethoxysilanes all gave a relatively sharp strong band near 10·8 eV that is probably due to the oxygen 2*p* lone-pair levels.

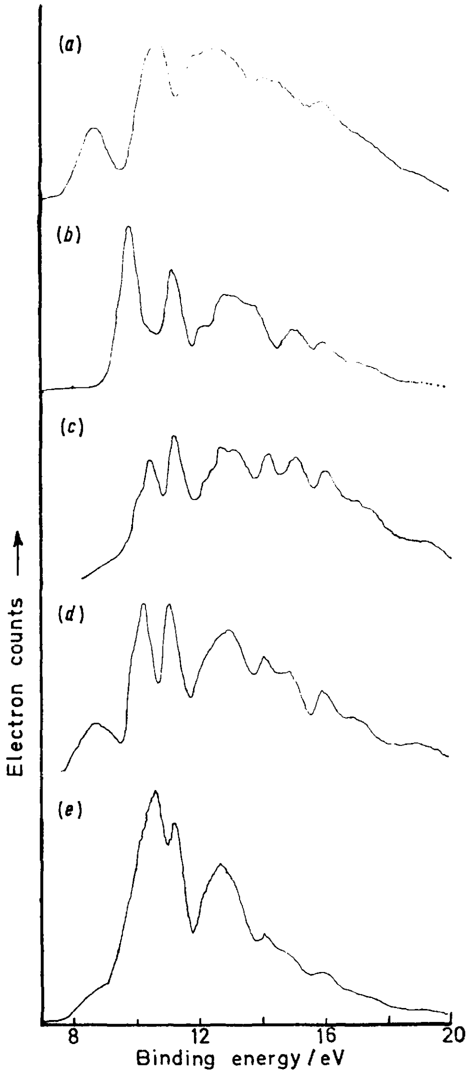

FIGURE 2 He(I) p.e. spectra of: (*a*) $(HOCH_2CH_2)_3N$; (*b*) $[N(CH_2CH_2O)_3]B$; (*c*) $[N(CH_2CH_2O)_3]SiH$; (*d*) $[N(CH_2CH_2O)_3]$-SiMe; (*e*) $[N(CH_2CH_2O)_3]Si(OEt)$

It is striking that only a single oxygen lone-pair band was observed in the spectra of tha itself and the triethoxysilanes. It appears that the three ethoxygroups in these molecules interact rather little, presumably because they are so flexible that the groups adopt conformations that minimise such interactions. The *two* strong bands in the spectra of (I) and (II) may then arise because of strong interactions between oxygen lone-pair levels imposed by the rigid structures of the molecules.

The nitrogen lone-pair levels may then be assigned to the isolated band at 8·7 eV in the spectrum of (I; R = Me) and to the shoulder at 10·1 eV in that of (I; R = H). In the spectrum of (II) it may well underlie the sharper band at 9·8 eV, giving rise to the apparently greater intensity of this band. It is difficult to be precise about the position of the nitrogen lone-pair band in the spectrum of (I; R = OEt), but it may contribute to the very gradual rise of the first band in the 9—10 eV region.

To analyse the interactions of the oxygen lone-pair levels with each other and with other levels we must consider the symmetry of the molecules. It seems likely that, as suggested by the crystal structures of (II)[3] and some more complex silatrans,[2] the only symmetry element present in the cage is a C_3 axis, the $-CH_2CH_2O-$ groups adopting a spiral conformation that allows for a minimum of angle strain at the saturated carbon atoms (Figure 3). The oxygen $2p$ lone pairs, one on each oxygen atom, then combine to give $A + E$ components relative to the three-fold axis, and the A component can interact with other levels of A symmetry such as the N lone pair and the Si–R bonding orbital in silatrans. (Had the molecular symmetry been C_{3v} the oxygen lone pairs would have given $A_2 + E$ combinations, and no interaction with the A_1 levels would have been possible.)

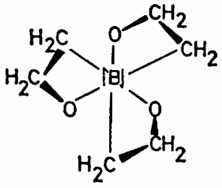

FIGURE 3

The E combination of oxygen lone-pair orbitals is unlikely to interact significantly with any other levels except perhaps the E combination of C–N σ-bonding orbitals. This remains unchanged throughout the series of molecules. We may then take the first of the two strong bands as representing this level, giving a marker whose position is related to that of an unperturbed oxygen level. The shifts of this marker will then be due to inductive and other effects that alter the net charge on the oxygen atoms. All the silatran spectra show this band at 10·4 ± 0·2 eV, whereas it appears at 9·8 eV in the boratran spectrum. This difference probably indicates that σ-donation from N is considerably more effective to B than to Si. The boron atom thus acquires a significant negative charge which makes it effectively more electropositive relative to oxygen, leading to a higher negative charge on oxygen and a lower binding energy for the lone-pair levels.

The alternative assignment of the E level to the *second* strong band (11·1 ± 0·1 eV) in all the compounds is at first sight an attractive one. The corresponding level in a molecule of C_{3v} symmetry is the E combination, which is likely to be less antibonding than the A_2 combination. We believe that while it is perfectly possible that the oxygen–oxygen interaction would give an A level less tightly bound than the E level, the interaction of the A level with the N lone pair would be great enough to force the A level to higher binding energy than the E level. The first band would then still correspond to the E level. The shift of the other (A) component of the oxygen levels from the (E) marker position is then due to the interaction of the A level with the N lone-pair level and the interaction between the oxygen levels that leads to the A–E distinction. Unfortunately we have no way of knowing the size of this latter interaction, and indeed it seems likely that it will alter within our set of molecules, depending as it must on the exact conformation within the spiral (Figure 3).

Two obvious assumptions that may be made are that the oxygen–oxygen interaction accounts for (*i*) all or (*ii*) none of the observed separation of the two bands. In the first case we may take the nitrogen level as essentially unperturbed by interaction with oxygen levels, giving the set of binding energies shown in Table 2, column (*i*). In the second case we must assume that all the observed splitting is due to interaction with the nitrogen level and correct the values of column (*i*) to give the values shown in column (*ii*) as the 'unperturbed' binding energy for the nitrogen lone pairs. The correction needed may of course be greater than that applied here if the A oxygen level is actually less tightly bound than the E level before interaction with the N lone pair. If the alternative assignment above, with the second strong band corresponding to the E level, is adopted, the close approach of the A to the N lone-pair level implies that their mutual interaction is extremely small. The values in column (*i*) are then appropriate. Neither set of figures is convincing in itself; it seems likely that the correct values will lie between those of columns (*i*) and (*ii*). It is then possible for the value for (II) to be significantly greater than that for (I), as expected from the observed effect on the oxygen lone-pair levels noted above.

TABLE 2

Nitrogen lone-pair binding energies (eV)

Compound	(*i*)	(*ii*)
$[N(CH_2CH_2O)_3]B$	*ca.* 10	*ca.* 11·3
$[N(CH_2CH_2O)_3]SiH$	10·1	10·9
$[N(CH_2CH_2O)_3]SiMe$	8·7	9·5
$[N(CH_2CH_2O)_3]Si(OEt)$	*ca.* 10	*ca.* 10·7

The interesting anomaly noted for (I; R = Me) remains. We suggest that this is due to an additional interaction with the Si–C bonding level (of A symmetry) expected near 11 eV, which depresses the observed value of the nitrogen lone-pair binding energy from near 10 eV to near 9 eV. The corresponding Si–H and Si–O bonding levels in (I; R = H and OEt) lie at rather higher binding energies, perhaps 12—13 eV, by analogy with similar bonds in other molecules. The interaction with the nitrogen lone-pair level will therefore be less important. An alternative interpretation of the anomaly would be to say that the strong inductive effect of the methyl group makes the silicon too strongly negatively charged to accept the nitrogen lone pair. We regard this as an oversimplified view, as this compound has the high dipole moment and low basicity characteristic of other silatrans.[1]

It is now clear that the nitrogen lone-pair levels in all the title compounds are significantly more tightly bound than that in tha. This indicates that the observed close approach of nitrogen to boron [3] or silicon [2] is in fact due to a bonding interaction involving the nitrogen lone-pair level. In (II) the acceptor orbital is certainly the vacant $2p_z$ orbital of boron; for (I) it is most likely to be largely derived from the vacant $3d_{z^2}$ orbital of silicon.

Conclusions.—We have observed a large increase in binding energy for the nitrogen lone-pair level in boratran and some silatrans. This shows that the close approach of the nitrogen atom to the boron or silicon atom in such compounds is associated with a bonding interaction of the nitrogen lone-pair level with vacant orbitals on boron or silicon.

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