Conformational Effects through Temperature Variation of Photoelectron Spectra

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Summary Temperature effects in photoelectron spectroscopy can be used to study electronic structure variation between conformational isomers; this is illustrated by reference to tetramethyl-diphosphine and some disubstituted ethanes.

Molecules which exist in more than one conformational isomer of different energy would be expected to show a temperature dependence in the photoelectron spectrum, provided the barrier to internal rotation is not too high. Several cases in which angle of twist about a single bond is reflected in the photoelectron spectrum have been reported,[1,2] and we now present examples in which the spectra of different conformational isomers can be distinguished by varying the temperature.†

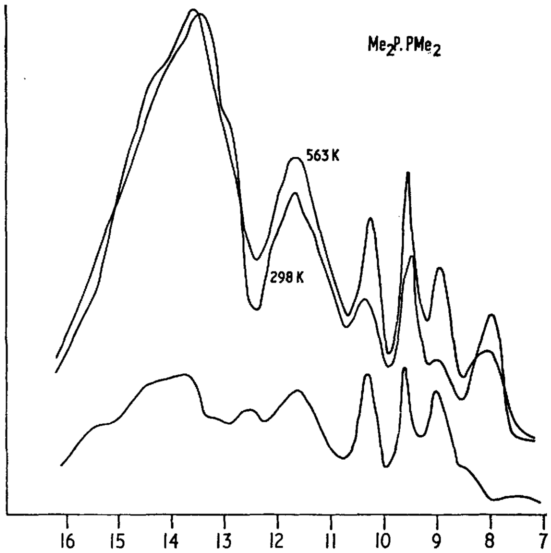

Figure 1. HeI photoelectron spectrum of tetramethyl diphosphine at two different temperatures (upper curves) and (below) the difference spectrum obtained after normalisation to the first band (which can be assigned unambiguously to the *trans*-rotamer). The abscissa scale is the ionization potential in electron volts.

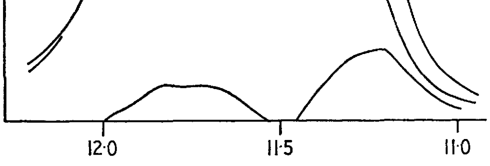

Figure 2. Part of the HeI photoelectron spectrum of 1,2-dichloroethane at two temperatures (above) and the difference after normalisation to the peak at 11·5 eV (below).

Part of the spectrum of tetramethyldiphosphine obtained at two temperatures is shown in Figure 1, together with a difference spectrum obtained by digital subtraction.

Dewar *et al.*[4] analysed the room temperature spectrum in terms of a suggested mixture of *trans*- and *gauche*-forms. In particular bands 1 and 3 (numbering from the highest electron energy) were taken as antisymmetric and sym-

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† The apparatus used in this work has been described[3] but the target chamber has been modified by addition of a nichrome ribbon electric heater. With this, photoelectron spectra could be obtained with chamber temperatures (measured by thermocouple) up to 573 K.

metric phosphorus $3p$ lone pair combinations in the *trans*-form with the band 2 being an unresolved mixture of the corresponding orbitals of the *gauche*-form. The temperature variation reported here shows, however, that in addition to bands 2 and 4 which increase with temperature as expected band 3 conceals a second component, 3′, which also increases with temperature (a sharp peak on the low electron energy side). The resultant band 2,3′ separation (0·6 eV) suggests a larger than expected[4] splitting for the lone pair interaction in the *gauche*-form. (A similar value has been suggested for the *gauche* lone pair $n_{\mathrm{N}_1} \rightarrow n_{\mathrm{N}_2}$ interaction in some cyclic hydrazines.[2])

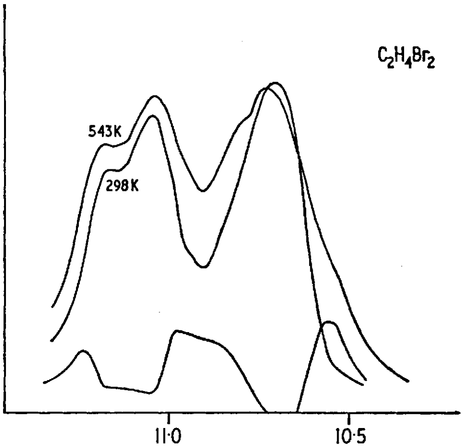

FIGURE 3. Part of the HeI photoelectron spectrum of 1,2-dibromoethane at two temperatures (above) and the difference after normalisation to the first peak (below).

Certain of the halogen-substituted ethanes show large temperature effects in the photoelectron spectrum over the range of temperatures up to 563 K (Figures 2, 3, 4). In each case the difference spectrum obtained showed four widely spread components in the energy range appropriate to lone-pair ionization. We assign these four bands to lone-pair ionization in the *gauche*-form. Comparison with the band spacings in the cold spectra in which the *trans*-form predominates suggest a generally larger interaction in the *gauche*-form though the extent to which this is a through-space or through-bond effect remains to be calculated. We note that the amounts of the *gauche*-form, as estimated from the relative peak heights in the high-temperature spectra, are rather less than expected from the enthalpy differences derived from earlier work.[5] This may be because the photoelectron experiment involves a continuous vapour flow in which equilibrium may not be completely attained.

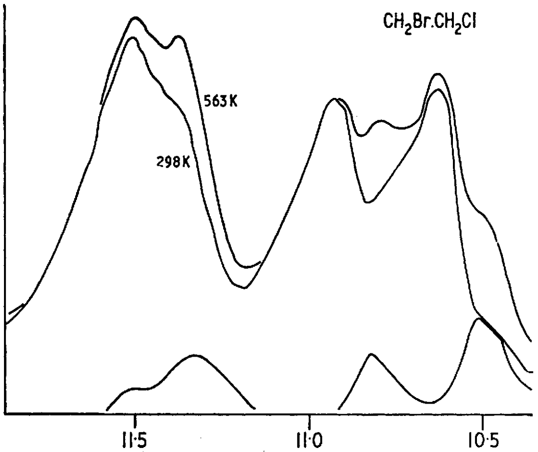

FIGURE 4. Part of the HeI photoelectron spectrum of 1-bromo-2-chloroethane at two temperatures (above) and the difference after normalisation to the second peak at 11·5 eV (below).

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