Photoelectron Spectra of Electron-rich Olefins and an Isostructural Boron Compound; Olefins of Exceptionally Low First Ionisation Potential

By B. CETINKAYA, G. H. KING, S. S. KRISHNAMURTHY, M. F. LAPPERT,* and J. B. PEDLEY
(*School of Molecular Sciences, University of Sussex, Brighton* BN1 9QJ)

Summary The photoelectron (P.E.) spectra of $C_2(NMe_2)_4$ and $\{C[N(Me)CH_2]_2\}_2$ each show five bands below 10·5 eV with the first vertical ionisation potential at 5·95 or 6·06 eV (*cf.*, C_2H_4, 10·5 eV; Na 5·1 eV), as is consistent with their strong reducing properties; these bands are assigned as π levels of various symmetries on the basis of (i) a good fit for experimental data with a simple Hückel calculation, and (ii) comparison of the spectra of the isostructural molecules $C_2(NMe_2)_4$ and $B_2(NMe_2)_4$.

ELECTRON-RICH olefins, such as enamines[1] and tetrakis-(dialkylamino)ethylenes [*e.g.*, $C_2(NMe_2)_4$][2] have a distinctive chemistry. For example, the latter compounds are reducing agents, and have a weak C–C bond, as exemplified[3] by reactions of certain of them with suitable transition metal substrates to afford metal–carbene complexes. These features are to be rationalised by bonding arguments and accordingly some P.E. spectra have now been examined.

We report the He(I) P.E. spectra of $C_2(NMe_2)_4$ and a related bischelate olefin recorded on a Perkin-Elmer PS16 instrument, modified for relatively involatile samples. The results, together with those on the isostructural $B_2(NMe_2)_4$, are shown in Figure 1. The energy levels (eV) for the highest occupied orbitals designated π_5–π_1 (π_5 is unoccupied in the boron compound) are: $C_2(NMe_2)_4$, −5·95, −7·5, −7·85, −8·5, −9·5; $\{C[N(Me)CH_2]_2\}_2$, −6·06, −8·4 (doubly degenerate), −9·1, −10·5; $B_2(NMe_2)_4$, −7·3, −7·6, −9·0, −9·5 (shoulder). Both molecules probably have the M_2N_4 (M = C or B) skeleton coplanar (i.r. spectral evidence for the boron compound,[4] and e.s.r. data[5] for the carbon radical cation), while steric interaction of methyl groups attached to the nitrogen atoms causes twisting about the M–N bonds, although the configuration at each nitrogen is approximately trigonal.

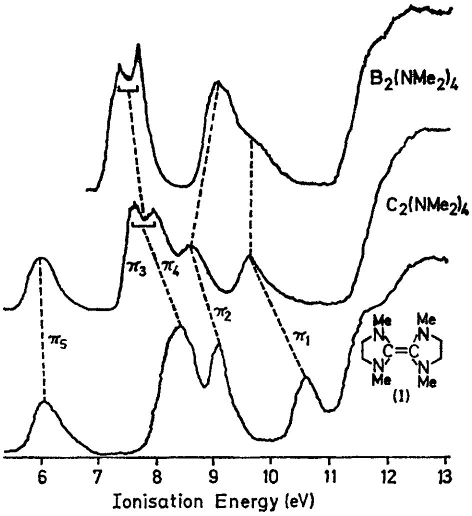

FIGURE 1. He(I) *Photoelectron spectra.*

The experimental data lead (Figure 2) to acceptable Hückel parameters for the π system: α_C −6·1, α_B −4·5, α_N −7·7, β_{CC} −1·6, β_{BB} −0·9, β_{CN} −1·3, and β_{BN} −2·0. In simple Hückel theory orbitals π_3 and π_4 are taken as degenerate and therefore from the mean of these and π_1, π_2, and π_5 a unique set of Hückel parameters is derived; whereas for the boron compound one of the four parameters must be arbitrarily defined. Thus α_B was taken as −4·5, because it seemed reasonable on grounds of atomic electronegativities and I.P.s that α_C is intermediate between α_B and α_N. In Figure 2 the π-M.O.s (π_1 − π_6) are shown as appropriate linear combinations of M_2 (π and π^*) and degenerate nitrogen $p\pi$ orbitals. The various symmetries of $\pi(M_2)$, $\pi^*(M_2)$, and π_1 − π_6 are indicated by reference to the constituent A.O.s, where empty and solid circles indicate directions of the positive lobes of the p-orbitals.

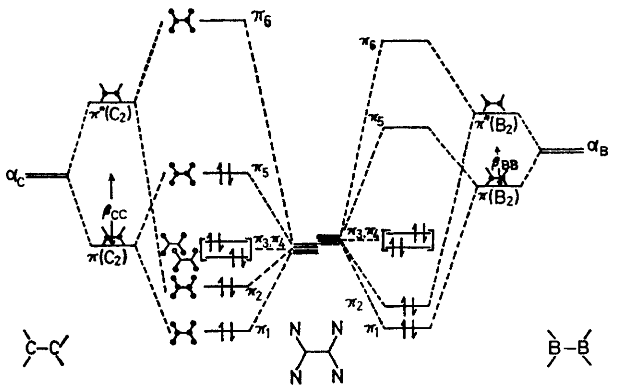

FIGURE 2. *Schematic energy levels for* $C_2(NMe_2)_4$ *and* $B_2(NMe_2)_4$.

Some of the correlations between P.E. data and theory (see Figures 1 and 2) are as follows. (i) The orbital π_1, being bonding over six centres, has the appropriate broad and fairly symmetrical P.E. band. (ii) That $|\beta_{BN}|$ is greater than $|\beta_{CN}|$, is consistent with the B–N π-bond being stronger than the CN (N → B back-donation). (iii) That $|\beta_{BB}|$ is smaller than $|\beta_{CC}|$ is consistent with the B–B bond being longer than the C–C. (iv) Consistent with (ii) and (iii) is the experimental observation that π_2 is lower in energy for the boron compound. (v) In Hückel theory π_3 and π_4 (which are essentially nitrogen non-bonding $p\pi$ orbitals, as is consistent with the partially resolved narrow P.E. bands) are degenerate. However, *N,N*-non-bonding interactions are different for each of π_3 and π_4 and hence two bands are observed, except in $\{C[N(Me)CH_2]_2\}_2$. These interactions depend on *N,N* distances which will differ in the two olefins because of the constraining effect of the chelate ring in $\{C[N(Me)CH_2]_2\}_2$. (vi) The orbital π_5 is antibonding (as is consistent with the broad P.E. band) between four of its six centres and is therefore high in energy; it is occupied only in the carbon compounds which therefore explains their low 1st I.P. (and hence the readiness with which they form radical cations, dications, and behave as reducing agents).[1, 2] (vii) As π_5 is unoccupied in $B_2(NMe_2)_4$, the only filled π orbital which is B–B bonding is π_1, which in any case has more *N*- than *B*- character; this is consistent with a long B–B bond distance and leads to the prediction that $[B_2(NMe_2)_4]^{2-}$ should be readily formed and that its B–B bond length should be substantially reduced while the B–N bond lengths be increased. (viii) It is noteworthy that $(\alpha_C + \beta_{CC})(\pi_{C2})$, in $C_2(NMe_2)_4$ ($-7{\cdot}7$ eV) is much higher than in C_2H_4 ($-10{\cdot}5$ eV); this can only in small part be due to a difference in β_{CC}, as β_{CC} values are small. A major effect must be a destabilisation of all π-levels in the electron-rich olefins caused by interaction with lower-lying π systems constituted from the methyl substituents on nitrogen. While it would be incorrect to relate β_{CC} values in the two olefins directly to their C–C bond dissociation energies ($\gg$ for C_2H_4), the difference for the two compounds may significantly be due to greater stabilisation of the carbene with Me_2N substituents rather than H.

That the remarkable influence of the Me_2N substituents in lowering the 1st I.P. from 10·5 eV in C_2H_4 to 5·95 eV (the lowest ever 1st I.P. published for a spin-paired system)[6] in $C_2(NMe_2)_4$ is attributable to π rather than σ effects is consistent with Taft-type substituent constants: thus the group Me_2N is known to exercise the largest of all $+M$ effects [σ_p $-0{\cdot}83$, σ_p^+ $-1{\cdot}8$, $(\sigma_p^+ - \sigma_p)$ $-0{\cdot}97$],[7] but a small $-I$ effect (σ_i $+0{\cdot}10$).[8] These 1st I.P. data may be compared with those on C_2F_4 (10·5 eV),[9] C_2Cl_4 (9·5 eV),[9] C_2Me_4 (8·53 eV),[10] $C_2(R)_3H$ (R Me or Me_3Si, 8·85 eV),[11] and *trans*-$[Me_3SiCH_2(H)C]_2$ (7·95 eV).[11] Other substituents which might be expected significantly to lower I.P.s of olefins are SMe (σ_p 0·00, σ_p^+ $-0{\cdot}60$) and to a lesser extent OMe (σ_p $-0{\cdot}27$, σ_p^+ $-0{\cdot}78$).

In view of the massive effect that four *N*-substituents have on the energy levels of an olefin, it is interesting to learn the influence of other substituents, and of less than four substituents. Preliminary results on the enamine[12] derived from pyrrolidine and cyclohexanone, show a first vertical I.P. of 7·1 eV which indicates that the first *N*-substitution has the major effect in reducing the I.P.s of C_2H_4.

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