He I Photoelectron Spectra of Unstable Boron Isocyanates; Electronic and Geometric Structures in the $BCl_x(NCO)_{3-x}$ Series†

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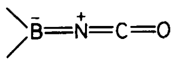
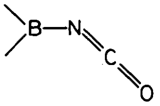
He I photoelectron spectra have been recorded for the series of unstable boron isocyanate molecules $BCl_2(NCO)$, $BCl(NCO)_2$, and $B(NCO)_3$, obtained in a low-pressure flow system from the reaction of gaseous BCl_3 with solid AgNCO at moderate temperatures. Trends in orbital energies can be tracked through the series BCl_3 to $B(NCO)_3$, thereby providing information on the relative π-bonding capability of the NCO and Cl moieties. These trends can also be followed by semiempirical modified neglect of diatomic overlap calculations. The optimised structures and photoelectron spectra of these molecules support the tendency toward non-linear BNCO chains with increasing NCO substitution, such that $B(NCO)_3$ has a C_{3h} structure.

Isocyanates of main group elements, attached through nitrogen as M–NCO (in preference to the cyanates M–OCN), have a long history, principally because of their interesting chemistry,[1,2] bonding and structure,[3] including the possibility of M–NCO linear or quasilinear (*e.g.* H_3SiNCO) and bent (at nitrogen) structures.‡ [2,3] Off-axis substitution on an isocyanate, thiocyanate, or azide group is generally the norm, leading to interesting spectroscopic properties caused by a splitting of the π degeneracies. Thus ultraviolet photoelectron spectroscopy (u.p.s.) of a series of XNCO molecules (X = hydrogen, halogen, methyl, cyano, *etc.*) has been performed and interpreted on this basis.[4–7] In this work we consider isocyanates of boron for which there is a paucity of data due to the instability of the discrete species (*e.g.* polymerisation), and the general tendency, as with many trigonal boron compounds, to disproportionate.[8,9] Some synthetic and spectroscopic studies have, however, been reported for the corresponding isothiocyanates, M–NCS, usually within mixtures, substituted primarily by Me, SMe, Cl, Br, and I.[10–12]

Our interest is in following the trends in ligand (Cl and NCO) orbital energies with successive NCO substitution, from the D_{3h} BCl_3 molecule, through possible C_{2v}- or C_s-like mono- and di-substituted species, to D_{3h}, C_{3h}, or C_s $B(NCO)_3$, and attempting to establish the geometric structures of this series of boron isocyanate molecules. Of particular concern is the question of linearity (or lack of it) in the BNCO chain(s), since two resonance forms, *e.g.*,





can be envisaged. It might be anticipated that p_π donation from N would favour the linear configuration, and associated planarity. To this end, it has recently been reported that $BCl_2(NCO)$ in solution has a linear BNCO group from interpretation of i.r. data,[8] a conclusion similar to the establishment by i.r. spectroscopy of a C_{2v} structure for $BMe_2(NCO)$.[13] Conversely, competing p_π donation from the halogen will reduce the extent of BN π bonding [compare *e.g.* halogen substitution in the $BX_2(NH_2)$ series[14]]. In addition, if bent structures are adopted, additional attention must include the conformations and relative energies of the bis(isocyanato)-species, $BCl(NCO)_2$, with U or W C_{2v} structures, or a sickle C_s structure, and the tris(isocyanato)-species, $B(NCO)_3$, with a C_{3h} structure, *versus* D_{3h} or C_s structures.

Experimental

The boron isocyanates were prepared by reaction of gaseous BCl_3 (Matheson) with solid AgNCO (prepared by precipitation from aqueous solutions of KNCO and $AgNO_3$[15]) which was packed loosely into a Pyrex tube (internal diameter 8 mm). The apparatus was attached directly to the ionisation chamber of a fast-pumping photoelectron spectrometer, and the AgNCO dried under vacuum at *ca.* 100 °C for a few hours. Boron trichloride at *ca.* 0.1 Torr (*ca.* 13.3 Pa) was then flowed slowly over the heated solid; with fresh AgNCO the extent of replacement of Cl by AgNCO can be tuned according to temperature. Thus, below 40 °C the sole product was the starting material BCl_3, whereas at 50—70 °C a mixture of BCl_3 and $BCl_2(NCO)$ was obtained, followed by mixtures involving three species, giving finally, at *ca.* 100 °C, pure $B(NCO)_3$. Pure spectra of $BCl(NCO)_2$ and $BCl_2(NCO)$ could not be obtained; however, as illustrated below, there are unique bands that provide the basis for spectral stripping. It should also be noted that with use the AgNCO loses its efficacy, and the temperature has to be increased by some 10—30 °C to maintain the efficiency of the isocyanate replacement reaction.

He I spectra were recorded on a home-built instrument[16] with digital data acquisition *via* a PC/XT computer.[17] Resolution was 40 meV during the course of the experiments, and spectra were calibrated with the known ionisation potentials (i.p.s.) of MeI, HCl, and Ar.

Semiempirical calculations employing the modified neglect of diatomic overlap (MNDO) Hamiltonian for heats of formation, optimised structures, and eigenvalues were performed on a SUN 3/160 workstation using the MOPAC suite of programs.[18a,§]

Results

The photoelectron spectra of the BCl_3/AgNCO reaction as a function of temperature are shown in Figure 1. With increasing

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† *Non-S.I. unit employed:* eV ≈ 1.60×10^{-19} J.

‡ There is also considerable evidence for non-linearity in the NCO group, which is typically bent away by 5—10°.

§ The PRECISE option was used, as suggested recently.[18b]

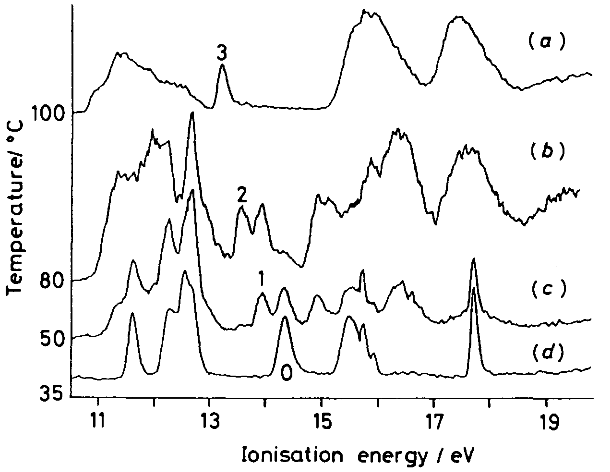

Figure 1. He I photoelectron spectra of the BCl_3/AgNCO reaction as a function of temperature. The peaks between 13 and 15 eV are labelled 0, 1, 2, and 3, corresponding to the BCl_xN_{3-x} π-bonding orbital (a_2'' or a'') in molecules with 0 through to 3 NCO groups. Mixtures are evident for partial Cl replacement by NCO. (*a*) $B(NCO)_3$, (*b*) $BCl(NCO)_2$ + $BCl_2(NCO)$; (*c*) BCl_3 + $BCl_2(NCO)$; and (*d*) BCl_3

Table. Experimental i.p.s. (±0.05 eV unless otherwise stated) of $BCl_2(NCO)$, $BCl(NCO)_2$, and $B(NCO)_3$

$BCl_2(NCO)$	$BCl(NCO)_2$	$B(NCO)_3$	Approximate description
11.6	11.51	11.15	NCO (non-bonding) and Cl
11.85	12.12	11.53	
12.37	12.12	11.99	
12.80	13.02	12.4	
14.03	13.67	13.30	a''
14.98	15.3	—	B-Cl σ
16.45	16.2	15.85	NCO(bonding)
17.6	17.6	17.45	NCO p_σ

temperature the relatively sharp bands due to Cl 3*p* orbitals are replaced by broader bands corresponding to NCO π non-bonding and bonding orbitals. A unique feature, however, is the series of sharp bands which gradually shifts from 14.4 eV in BCl_3 to 13.3 eV in $B(NCO)_3$; these are indicative of the relative proportions of the four species, and permit reasonably accurate digital subtraction in order to extract photoelectron spectra of 'pure' isocyanates (Figure 2). Ionisation potentials for the three isocyanate species are reported in the Table.

Discussion

Structures.—Before discussing trends and assignments in the series, it is instructive to consider the conformations of these molecules so that the calculated i.p.s can be compared (assuming Koopmans' theorem) to the experimental results. The calculated structures for all three molecules with both fixed linear and non-linear BNCO chains are shown in Figure 3, together with their associated heats of formation (ΔH_f); these calculations were fully optimised within a particular symmetry representation. Planarity was imposed in all cases since non-planar structures were found not to be important.

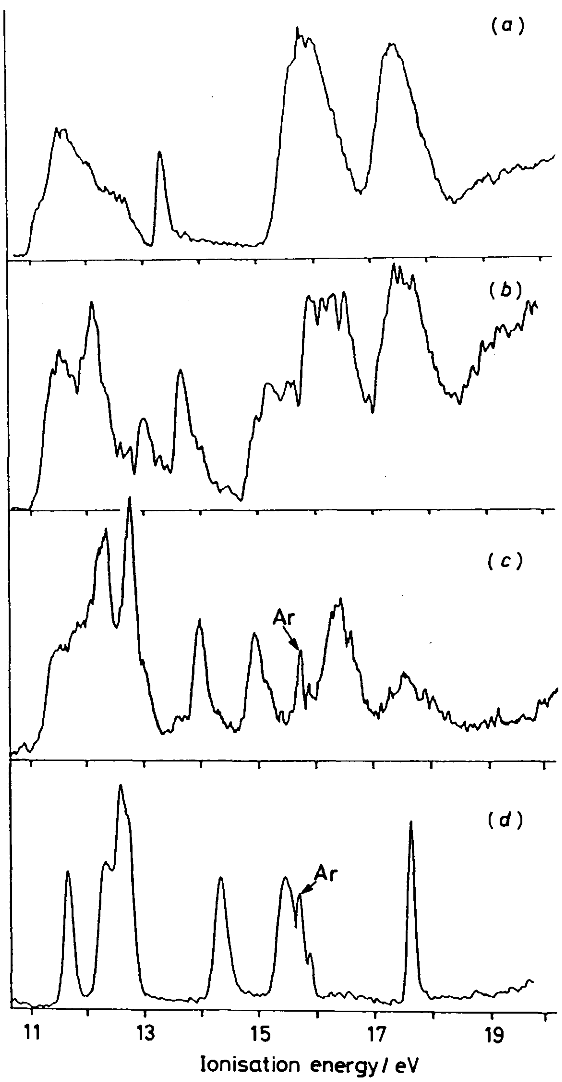

Figure 2. Photoelectron spectra following spectral stripping of the mixtures: (*a*) $B(NCO)_3$; (*b*) $BCl(NCO)_2$; (*c*) $BCl_2(NCO)$; and (*d*) BCl_3

It is apparent from these results that structures with bent BNC angles (132—147°) are the more stable at this level of theory, and all such structures also show a *trans*-bent NCO group to the extent of some 12°. The structures with linear BNCO groups are shown by frequency calculations to be transition states with the reaction co-ordinate involving bending at nitrogen. Hence, the sickle configuration (C_s) of $BCl(NCO)_2$ is preferred by 6.7 kJ mol^{-1} over the closest of the other two possibilities, and a C_{3h} structure for $B(NCO)_3$ is clearly favoured. Three other comments are in order. First, comparable calculations for HNCO and the analogue HNCS give angles qualitatively in agreement with known microwave data (*viz.* HNCO, calculated 120.2 *versus* 128°, experiment;[19] and HNCS, calculated 131.4 *versus* 135°, experiment[20]); calculation thus underestimates the angle. Secondly, for the direction $BCl_2(NCO)$ to $B(NCO)_3$ the structures become more bent at nitrogen; here it is difficult to separate steric effects (*e.g.* Cl ··· N non-bonded interactions) from electronic effects involving changes in π-bonding ability (Cl *versus* NCO), although the indications from the calculated structures are that NCO has more π-donating ability than does Cl. This notion is in accord with earlier conclusions based on displacement reactions,[9] and is supported by the calculated π-electron

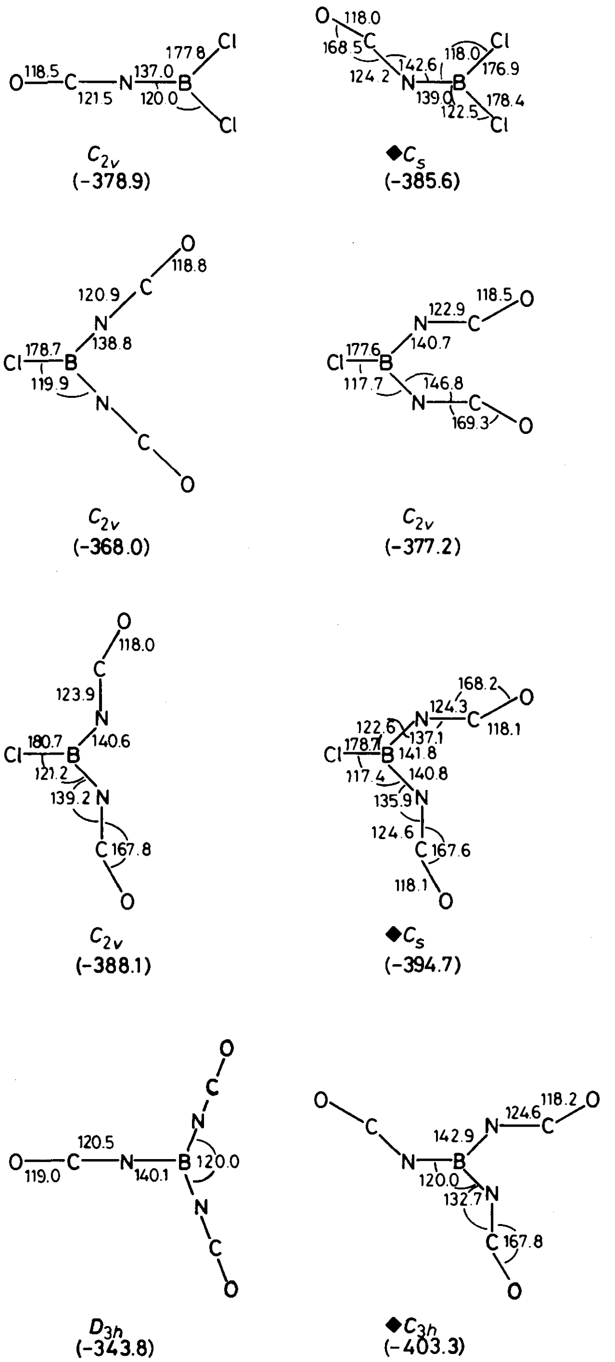

Figure 3. Calculated (MNDO) structures and heats of formation (values in parentheses) for linear and non-linear BNCO groups in $BCl_2(NCO)$, $BCl(NCO)_2$, and $B(NCO)_3$: ΔH_f in kJ mol^{-1}, bond lengths in pm, and angles in °. The most stable structures are flagged by solid diamonds

densities on B, which increase with increasing NCO substitution. It is, however, important to point out that the individual BN bonds weaken with increasing NCO substitution, as evidenced by r_{BN} which increases from 139 to 142.9 pm upon NCO substitution (Figure 3). Thirdly, identical calculations (not shown) for the analogous isothiocyanate molecules indicate a trend towards linearity in all the NCS molecules [BNC angles in the range 163—179° from $B(NCS)_3$ to $BCl_2(NCS)$], which may indicate that the NCS group is a stronger π donor than is NCO. This statement must be tempered with the observation that all known molecules containing the NCS group have more linear M-NCS angles, and this may be simply an electronegativity effect. Indeed the calculated π-electron distribution on B is marginally less than in the NCO case, indicating the converse, in agreement with the ordering determined from displacement reactions.[9]

The question posed therefore is to what extent can we trust these calculations in terms of providing accurate gas-phase structures, and any subsequent conclusions regarding relative π-donor ability? At this level of theory, the NCS molecules appear to have linear or close to linear BNCS groups, whereas in the NCO case, despite the fact that MNDO seems to calculate the angle in HNCO some 8° too small, there is a clear distinction in energy between the bent and linear structures, (*e.g.* nearly 60 kJ mol^{-1} in the case of C_{3h} and D_{3h} $B(NCO)_3$. Some confidence in these conclusions can be provided by the u.p.s. results, which although not unambiguous from a structural point of view provide excellent agreement with the calculated orbital energies.

Assignments of Orbital Energies.—Up to the sharp B 2*s* orbital in BCl_3 (17.7 eV) there are eight i.p.s (counting degeneracies as two), which then increase by three with successive NCO insertion (loss of one σ and one π Cl orbital, and the gain of two non-bonding, two bonding, and one p_σ NCO orbital). Figure 2 shows this general trend in the loss of the relatively sharp Cl based orbitals and the development of broad bands in the 11—13 (slightly destabilised with respect to the Cl based orbitals) and 15—17 eV regions, corresponding to the NCO π_{nb} and π_b orbitals, respectively. An additional broad feature, increasing in intensity with NCO substitution, occurs around 17.5 eV and is associated with the NCO p_σ orbitals. Each of these three distinct regions corresponds more or less to those observed in the spectrum of the parent HNCO molecule.[4] What is not clear at present is the ability to distinguish any subtle splittings within a group of i.p.s, in order to establish whether or not the NCO group is linear; to this end we must compare our experimental results to calculation.

However, before we do this we note that the most interesting feature of the spectra involves the essentially monotonic destabilisation of the a_2'' π-bonding orbital in BCl_3 (14.35 eV[21]) as successive NCO groups are placed around the central boron atom. This destabilisation, amounting to 0.37 ± 0.01 eV per NCO group as N p_π character replaces Cl p_π, incurs very little change in the Franck–Condon envelope, and since the band in question lies in a relatively clean part of the spectrum it permits us to effect reasonably quantitative spectral subtractions.

Another notable feature, in contrast to the similarity of the π_b orbital, is the loss of the sharp peak associated with the B 2*s* orbital in BCl_3 even with substitution of only one NCO group. This is common in substitution of boron trihalides, since admixture of other *s* character shifts the i.p., and leads to much broader Franck–Condon envelopes. In fact, in this case we are unable to identify positively any bands associated with B 2*s* character, although the calculations (below) indicate a stabilisation due to the incorporation of C and O 2*s* character. It is feasible that weak structure in the 19—20 eV region could correspond to these i.p.s.

Comparison of Calculated Orbital Energies with Experiment.—Figure 4 shows the calculated orbital energies for BCl_3 and the three BNCO molecules at their optimised geometries (with non-linear BNCO chains); the connecting lines and labels indicate the general trends in orbital energies. Those orbitals corresponding to predominantly Cl 3*p* character can be matched to the relatively sharp peaks in the experimental spectra of $BCl_2(NCO)$ (12.37 and 12.80 eV) and $BCl(NCO)_2$ (13.02 eV), such that a comparison of Figures 2 and 4 demonstrates the increasing quantitative agreement of experiment with theory

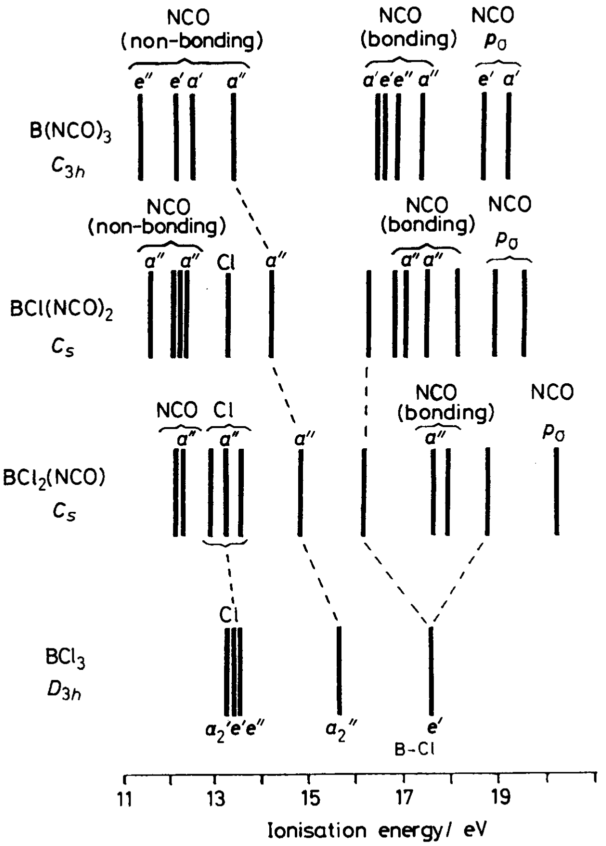

Figure 4. Calculated orbital energies for BCl_3 and the three isocyanate-substituted molecules at the optimised geometries. Symmetry labels indicate the π orbitals only for $BCl(NCO)_2$ and $BCl_2(NCO)$. Trends in orbitals of a specific type are indicated by dashed lines

upon NCO substitution. The values for BCl_3 are only qualitatively correct, the B 2*s* orbital (not shown) being calculated some 5 eV too high. In general the calculations do remarkably well in tracking the loss of Cl 3*p*, and the increase in NCO orbital character as discussed above. The trend most easily followed is that of the BCl_3 a_2'' orbital, which steadily destabilises upon NCO substitution from 14.4 (BCl_3) to 13.3 eV [$B(NCO)_3$]. The band of $BCl_2(NCO)$ at 14.98 eV corresponds to the B-Cl σ-bonding orbital, which is located at 14.95 eV in the unsubstituted BCl_2H molecule.[22]

In general it is not feasible to ascertain the gas-phase structure of these isocyanate molecules on the basis of comparison of experiment with calculations for linear or non-linear BNCO chains, except perhaps for $B(NCO)_3$. For $BCl(NCO)_2$ and $BCl_2(NCO)$ the difference between linear or non-linear eigenvalues is marginal, and does not permit any distinction to be made due to the broadness of the bands associated with the NCO orbitals. However, the relationship of experiment to theory bears additional scrutiny in the case of $B(NCO)_3$ for this is the structure predicted (see above) to have the most bent BNC angles. Here the computational result is in excellent quantitative agreement with experiment; it clearly shows the final emergence of the six NCO non-bonding orbitals in the 11—13.5 eV range, and the subsequent six bonding NCO and three $p_σ$ orbitals centred at 16.8 and 19 eV respectively. Figure 5 shows the spectrum of $B(NCO)_3$ together with the calculations for both the optimised C_{3h} structure, and the linear D_{3h} structure (which is shown by a frequency calculation to have the three negative eigenvalues corresponding to bending at N). The 11—13 eV region in the photoelectron spectrum shows a wide distribution of the NCO non-bonding orbitals; at least three or four separate maxima can be discerned in accord with the spread predicted for the non-linear C_{3h} structure. The calculation for the linear system shows a much tighter distribution and a predicted two maxima, and so the conclusion here is that $B(NCO)_3$ has non-linear BNCO groups.

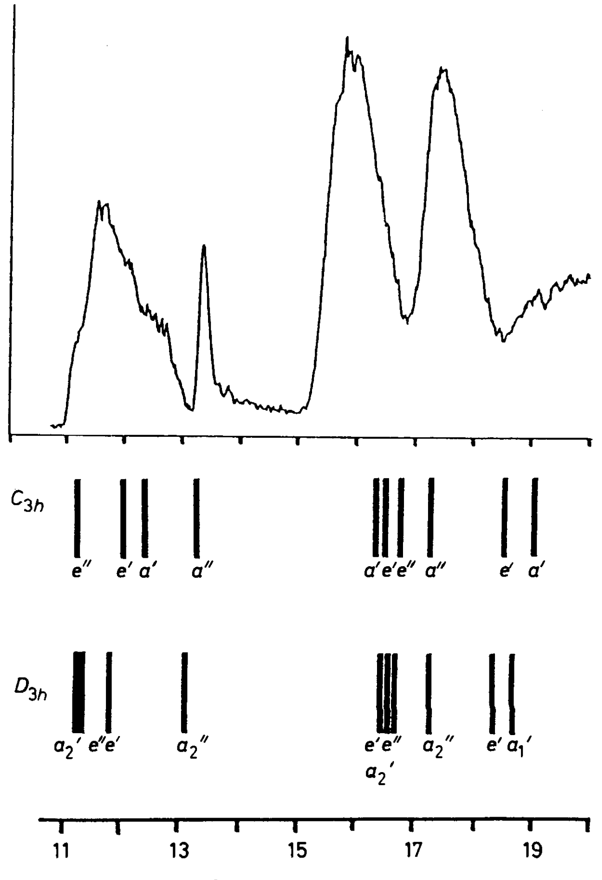

Figure 5. Comparison of the experimental photoelectron spectrum of $B(NCO)_3$ with the semiempirical calculations for structures involving linear (D_{3h}) and non-linear (C_{3h}) BNCO chains (see text for discussion)

This result is not unexpected in the sense that increasing NCO substitution (and a concomitant increase in π density on B) will weaken individual BN π bonding, leading to bent BNCO chains; the calculated BN bond orders confirm this trend. If, as a first approximation, the a_2''/a'' orbital can be taken as a measure of π stabilisation, then the observed shift of this orbital [which destabilises in the direction BCl_3 to $B(NCO)_3$] is in accord with these expectations.

Conclusions

The He I photoelectron spectra of the unstable $BCl_2(NCO)$, $BCl(NCO)_2$, and $B(NCO)_3$ molecules have been interpreted by following trends in the measured i.p.s, and a comparison with calculated orbital energies. Although the MNDO method suggests the presence of non-linear BNCO chains, unambiguous structures cannot, with confidence, be evaluated from the photoelectron spectra. However, it does appear that increasing isocyanation leads to loss of $p_π$–$p_π$ bonding between N and B, and an increasing trend toward non-linearity in the BNCO chain; this is supported by the photoelectron spectrum of $B(NCO)_3$ which points to a C_{3h} structure. Experiment and theory indicate a decrease in Lewis acidity from BCl_3 to $B(NCO)_3$.

Acknowledgements

N. P. C. W. thanks the Natural Sciences and Engineering Research Council of Canada for grants in support of this research.

References

1 M. F. Lappert and H. Pyszora, *Adv. Inorg. Chem. Radiochem.*, 1966, **9**, 133.
2 'The Chemistry of Cyanates and their Thio Derivatives,' ed. S. Patai, Wiley, New York, 1977.
3 C. Glidewell, *Inorg. Chim. Acta*, 1974, **11**, 257.
4 J. H. D. Eland, *Philos. Trans. R. Soc. London*, 1970, **268**, 87.
5 D. C. Frost, C. B. MacDonald, C. A. McDowell, and N. P. C. Westwood, *Chem. Phys.*, 1980, **47**, 111.
6 S. Cradock, E. A. V. Ebsworth, and J. D. Murdoch, *J. Chem. Soc., Faraday Trans. 2*, 1972, 86.
7 D. C. Frost, H. W. Kroto, C. A. McDowell, and N. P. C. Westwood, *J. Electron Spectrosc. Relat. Phenom.*, 1977, **11**, 147.
8 H. Mongeot, H. R. Atchekzai, M. Fouassier, and M. T. Forel, *J. Mol. Struct.*, 1980, **62**, 35.
9 M. F. Lappert, H. Pyszora, and M. Rieber, *J. Chem. Soc.*, 1965, 4256.
10 D. B. Sowerby, *J. Am. Chem. Soc.*, 1962, **84**, 1831.
11 J. Dazord, H. Mongeot, H. Atchekzai, and J. P. Tuchagues, *Can. J. Chem.*, 1976, **54**, 2135.
12 H-R. Atchekzai, H. Mongeot, J. Dazord, and J. P. Tuchagues, *Can. J. Chem.*, 1979, **57**, 1122.
13 J. Goubeau and H. Gräbner, *Chem. Ber.*, 1960, **93**, 1397.
14 C. A. Kingsmill, N. H. Werstiuk, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1987, **109**, 2870.
15 R. G. Neville and J. J. McGee, *Inorg. Synth.*, 1966, **8**, 23.
16 R. Sammynaiken, M.Sc. Thesis, University of Guelph, 1988.
17 M. Alaee, unpublished work.
18 (*a*) Quantum Chemistry Program Exchange, Indiana University, 1984, No. 455 (MOPAC); (*b*) D. B. Boyd, D. W. Smith, J. J. P. Stewart, and E. Wimmer, *J. Comput. Chem.*, 1988, **9**, 387.
19 W. H. Hocking, M. C. L. Gerry, and G. Winnewisser, *Can. J. Phys.*, 1975, **53**, 1869.
20 R. Kewley, K. V. L. N. Sastry, and M. Winnewisser, *J. Mol. Spectrosc.*, 1963, **19**, 975.
21 G. H. King, S. S. Krishnamurthy, M. F. Lappert, and J. B. Pedley, *Discuss. Faraday Soc.*, 1972, **54**, 70.
22 D. C. Frost, C. Kirby, C. A. McDowell, and N. P. C. Westwood, *J. Am. Chem. Soc.*, 1981, **103**, 4428.

Received 19*th August* 1989; *Paper* 9/03543E