The Electronic Structure of BC_3

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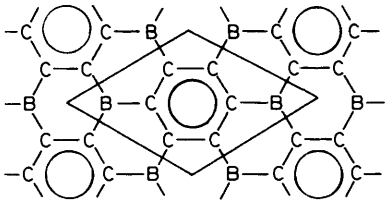
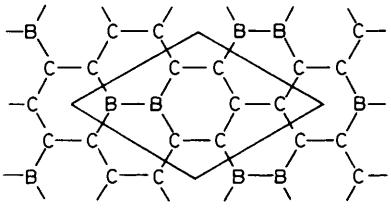
MNDO and extended Hückel calculations on the electronic structure of BC_3 based on structure (**1**) and the alternatives (**2**) and (**3**) suggest that (**1**) would be an insulator rather than show metallic conductivity but that structures (**2**) and (**3**) could explain its high conductivity.

Bartlett and his co-workers[1—3] have synthesised BC_3 from interaction of BCl_3 with benzene, and have suggested a graphite-like structure (**1**). The conductivity of BC_3 was reported to be greater than that of graphite ($2 \times 10^4\ \Omega^{-1}\ cm^{-1}$).[1] Assuming that this material exhibits defect-free bulk solid properties, we have carried out MNDO[4] and extended Hückel theory[5] (EHT) energy band calculations on BC_3 based on structure (**1**) and the alternatives (**2**) and (**3**), and suggest plausible electronic structures to explain the unusually high conductivity of BC_3.

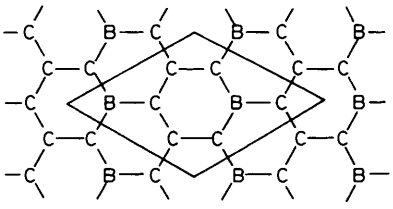
With low levels of chemical doping, holes or extra conduction electrons are created within the band structure leading to the charge carriers, whereas periodic chemical substitution has a different effect; the periodic perturbation may create an energy gap, just as the bond length alternation does for polyacetylene.[5] Whether the periodic substitution induces any energy gap opening can only be determined by calculation. We have thus carried out calculations on the boron substituted graphite-like structures and the resulting E_g values for these structures were found to be as follows: structure (**1**) of BC_3 is an insulator (E_g 1.4—1.8 eV), while the alternatives (**2**) and (**3**) are semi-metallic (E_g 0.2 eV) and metallic (E_g 0.0 eV), respectively. The band structures of (**1**)—(**3**) were derived from that of graphite having a zero E_g value, with eight carbon atoms in the unit cell.[6] Even though the models and methods used are approximate, the qualitative conclusions should have some general validity.



(**1**)



(**2**)



(**3**)

All the band structure calculations were performed with the extended Hückel method,† with all B–C and C–C bond distances assumed to be equal to 1.42 Å. A further refined calculation on structure (**1**), using the solid state version[4b] of the MNDO self-consistent field model, which is capable of geometry optimisation, gave C–C and B–C bond distances of 1.424 and 1.546 Å, respectively. Using these optimised parameters in an extended Hückel band calculation (MNDO is very good at predicting geometry, but cannot be used for band structures), we obtained an E_g value of 1.8 eV for structure (**1**).

Similar trends in E_g values are observed for the nitrogen-substituted compounds, NC_3, with 10π electrons per unit cell.

In summary, band gaps of both boron- and nitrogen-substituted graphite depend upon the topology and the chemical constitution of the unit cell, as well as the electron count. Based on our band calculations, we propose the alternative structures (**2**) and (**3**) for BC_3. The semi-metallic or metallic character of these structure is in line with the high conductivity of BC_3.

This work has been partially supported by the Camille and Henry Dreyfus Foundation, and by the National Science Foundation (DMR-8702148). M. K. is a Camille and Henry Dreyfus Teacher-Scholar (1984—1989).

Received, 26th June 1987; Com. 903

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† Parameters for EHT were taken from ref. 5. The π ionization potentials (IP) are, accordingly B: −8.5 eV, C: −11.4 eV, N: −13.4 eV.