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# A theoretical study of the rearrangement processes of energized CCCB and CCCAl†

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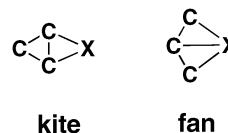
The rearrangement reactions of energized CCCB and CCCAl have been studied by means of quantum mechanical electronic structure calculations. Potential barriers were determined at UCCSD(T)/aug-cc-pVTZ with optimized molecular geometries and harmonic vibrational frequencies determined at the UB3LYP/6-311+G(3df) level. Two planar fully cyclized isomers are key intermediates in both systems. One of these is the “rhombic” structure, (analogous to rhombic  $C_4$ ) which is called the “kite” isomer. The other fully cyclized structure is called the “fan” structure. The quartets of CCCB and CCBC are the ground states of these structures [by 49.8 and 7.9  $\text{kJ mol}^{-1}$  ( $E$  values), respectively], whereas the ground state of kite  $C_3B$  is the doublet (by 131.8  $\text{kJ mol}^{-1}$ ). The rearrangement of doublet CCCB is more energetically favourable than that of the quartet, with a maximum barrier of +68.6  $\text{kJ mol}^{-1}$  together with the formation of fan  $C_3B$  (−60.7  $\text{kJ mol}^{-1}$ ), and then CCBC (+40.6  $\text{kJ mol}^{-1}$ ). Quartet CCCB rearranges through fan  $C_3B$  (+31.4  $\text{kJ mol}^{-1}$ ) to give CCBC (+82.8  $\text{kJ mol}^{-1}$ ) over a maximum barrier of +184.9  $\text{kJ mol}^{-1}$ . The  $C_3Al$  system is different from  $C_3B$  in a number of ways. Doublet CCCAl is the ground state (by 116.3  $\text{kJ mol}^{-1}$ ) and rearrangement to fan  $C_3Al$  requires only 21.8  $\text{kJ mol}^{-1}$  of excess energy. Fan  $C_3Al$  (+18.8  $\text{kJ mol}^{-1}$ ) then converts to the kite isomer (−12.1  $\text{kJ mol}^{-1}$ ) over a barrier of 50.2  $\text{kJ mol}^{-1}$ . Conversion to CCAIC is energetically unfavourable requiring some 371  $\text{kJ mol}^{-1}$  of excess energy [at the UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311+G(3df) level of theory]. Rearrangement of quartet CCCAl is more complex, but again, the cyclic kite and fan forms are in equilibrium and ring opening to CCAIC is unfavourable.

## Introduction

The chemistry of carbon clusters including cumulenes has been reviewed.<sup>1</sup> The importance of cumulenes in interstellar chemistry<sup>2</sup> and in flames<sup>3–5</sup> has been described. Our particular interest in this area has involved the rearrangement processes of energized CCCC,<sup>6</sup> CCCSi,<sup>7</sup> CCCN,<sup>8</sup> CCCP,<sup>7</sup> CCCO,<sup>9</sup> and CCCS.<sup>9</sup> These linear CCCX systems (except CCCSi and CCCP) are known interstellar molecules having been identified in molecular clouds, interstellar ice and/or circumstellar envelopes.<sup>10</sup> The systems CCCC,<sup>6</sup> CCCN,<sup>8</sup> CCCO,<sup>9</sup> and CCCS<sup>9</sup> have been synthesized by unequivocal routes in the tandem collision cell system of a VG ZAB 2HF mass spectrometer and their reactions studied using a combination of the charge reversal ( $^-CR^+$ )<sup>11,12</sup> and neutralization reionization ( $^-NR^+$ )<sup>13,14</sup> techniques. The reaction coordinates of the rearrangement processes of these systems have been studied at the

CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory.<sup>8,9</sup>

In contrast, no unequivocal synthetic procedures were available to form CCCSi and CCCP, and these two systems were studied purely from a theoretical viewpoint.<sup>7</sup> The key rearrangement process of energized CCCC, CCCSi, CCCN and CCCP is the conversion of the linear system to a stable “rhomboid” system (only truly rhomboid for  $C_4$ ), cleavage of which will effect at least partial scrambling of the C skeleton. In certain cases a second planar cyclic structure can be formed and sometimes the two cyclic structures are interconvertible. To avoid confusion between these two planar structures, we now adopt the nomenclature used by Bates *et al.*<sup>15</sup> The “rhomboid” structure is called a “kite”, with the other cyclic structure called a “fan” (see below). The final systems to be studied were linear CCCO and CCCS and they behave differently to the systems just described. In these cases, bond cleavage processes are more energetically favourable than cyclization to “rhombic” (kite) or fan systems, with CCCO and CCCS decomposing to CC and CO, and CCC and S, respectively.<sup>9</sup>



The planar cyclic structures are both unusual and interesting. They are relatively stable species (with respect to the linear

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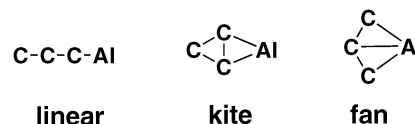
† Electronic supplementary information (ESI) available: Table S3: quartet  $C_3B$  potential surface. Table S4: doublet  $C_3B$  potential surface. Table S5: doublet  $C_3Al$  potential surface. Tables S6 and S7: quartet  $C_3Al$  potential surface. Tables S8 and S9: selected minima structures of  $C_3B$  and  $C_3Al$  calculated at different theory levels. Table S10: standard (calculated) enthalpies of formation for  $C_3B$  and  $C_3Al$  isomers. Tables S11 and S12: charge distributions of selected  $C_3B$  and  $C_3Al$  isomers determined by different methods. See DOI: 10.1039/b906345e

CCCX structures); kite (“rhombus”)  $C_3Si$  has already been identified in the evolved carbon star system IRC + 10216,<sup>16,17</sup> and it seems likely that rhombus  $C_4$  should also be present in interstellar regions. The CCCX systems, where X represents the elements of groups 4, 5 and 6 in periods 2 and 3 of the Mendeleev periodic classification, have already been studied. It would be interesting to extend this investigation to group 3, namely to study the behaviour of CCCB and CCCAl. Our interest in these systems is not just from a possible interstellar viewpoint (AlCl, AlF and AlNC have already been detected in inner circumstellar envelopes of carbon-rich stars<sup>18,19</sup>) but also for other reasons. Linear CCCB and CCCAl are known to be stable (see below), but when energized can they interconvert into kite and fan cyclic systems? These molecules are also of interest because both boron and aluminium are well known high density materials, have been used as components of fuels, propellants *etc.*,<sup>20–23</sup> and the use of cognate systems, particularly those using these elements together with carbon, is currently being developed.<sup>24–27</sup>

Studies of  $C_nB$  systems have already been reported, mostly concerning boron carbide (BC) and  $BC_2$ .<sup>28–38</sup> Both synthetic and theoretical work has been reported for  $BC$ ,<sup>28,29,31,32,36,38</sup>  $BC^-$ ,<sup>34</sup>  $CCB$ ,<sup>34,35,37,38</sup>  $CCB^-$ ,<sup>33,38</sup> and  $CBC$ .<sup>30</sup> There are fewer reports of higher borocumulenes, but  $C_nB$  systems have been generated in laser experiments,<sup>39</sup> as have the anions<sup>40,41</sup> and theoretical studies have been reported for these systems.<sup>39–41</sup> Vibrational spectra and theoretical calculations have been reported for  $C_3B$ .<sup>42</sup> Some more complex boron systems have been reported, including theoretical studies of the interconversion of  $C_4B^{43}$  and  $H_2C_4B$  isomers,<sup>44</sup> together with the formation of  $CCBO$ ,<sup>45</sup>  $CCCCBO$ <sup>46</sup> and  $OCBBCO$ .<sup>47</sup>

The AlC molecule has been extensively studied by theorists<sup>48–51</sup> and experimentalists,<sup>49,51–53</sup> as have  $AlC^-$ ,<sup>54,55</sup>  $C_2Al$ <sup>15,51,56–61</sup> and  $C_2Al^-$ .<sup>55</sup>  $C_2Al$  is predicted to have an ionic  $Al^+C_2^-$  electronic structure<sup>51</sup> with T shaped geometry.<sup>15,57–61</sup>  $C_3Al$  has been made by evaporation of aluminium and carbon rods in solid argon at 10 K, and FT IR spectra have been reported.<sup>15</sup> There have been many theoretical investigations of the  $AlC_3$  system.<sup>56,60,62–65</sup> It is reported that there are three low-lying isomers of  $AlC_3$ ,<sup>15,56,60</sup> namely the linear system and the kite and fan cyclic structures. Zheng *et al.* report<sup>61</sup> that the lowest energy isomer of  $AlC_3$  is the kite quartet, whereas Barrientos *et al.*<sup>56</sup> consider that the three structures shown

below have doublet ground states, with the doublet linear species being the lowest energy isomer. The charged species  $C_3Al^+$ <sup>64</sup> and  $C_3Al^-$ <sup>63,65</sup> have also been studied.



Since it is not possible to use unequivocal synthetic approaches [of the type we have used for other CCCX (X = C, N, O and S) systems<sup>6–9</sup>] for CCCB and CCCAl, the aims of the present study are: (1) to use high level theoretical calculations to investigate whether radicals CCCB can rearrange to CCBC through cyclic isomers. Such interconversions have not been studied experimentally or theoretically previously; (2) to use theoretical calculations to compare the chemistry of radical CCCAl with that of CCCB.

## Computational methods

Primary data for this investigation were obtained using geometry optimizations carried out at the spin-unrestricted version of the Becke 3LYP method<sup>66,67</sup> designated UB3LYP with the split-valence 6-311+G(3df) basis set. Stationary points were determined by calculation of the frequencies using analytical gradient procedures, according to the principle of either minima (no imaginary frequencies) or transition states (one imaginary frequency). The minima connected by a given transition structure were confirmed by intrinsic reaction coordinate (IRC) calculations. Single-point (frozen core) coupled-cluster calculations including all single- and double-excitations, based on a reference UHF single determinant, together with a perturbative treatment of all connected triple-excitations,<sup>68</sup> designated UCCSD(T), were carried out with the aug-cc-pVTZ basis set to calculate the energies.<sup>69,70</sup> Zero-point vibrational energies (ZPVEs) were determined from the harmonic vibrational frequencies calculated at the UB3LYP/6-311+G(3df) level. Total energies at 0 K were obtained by the sum of the UCCSD(T)/aug-cc-pVTZ energy and ZPVE correction (unscaled). The enthalpies of formation of different species at 298 K were obtained by standard methods.<sup>71</sup> Data obtained using the UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311+G(3df) level of

**Table 1** Energies (hartree), relative energies (kJ mol<sup>−1</sup>) and UCCSD(T) CBS limits (hartree) of doublet and quartet linear, kite and fan isomers of  $C_3B$

Level of theory	<sup>2</sup> Linear	<sup>4</sup> Linear	<sup>2</sup> Kite	<sup>4</sup> Kite	<sup>2</sup> Fan	<sup>4</sup> Fan
UCCSD(T)/aug-cc-pVDZ//UB3LYP/6-31+G(d)	−138.43637 (+79.8)	−138.44884 (+47.0)	−138.46675 (0)	−138.41349 (+134.6)	−138.45111 (+41.0)	−138.43526 (+82.7)
UCCSD(T)aug-cc-pVTZ//UB3LYP/6-311+G(3df)	−138.53113 (+99.2)	−138.55013 (+49.3)	−138.56890 (0)	−138.51868 (+131.8)	−138.55423 (+38.5)	−138.53817 (+80.7)
UCCSD(T)/cc-pVQZ//UB3LYP/6-311+G(3df)	−138.55708 (+104.9)	−138.55708 (+53.2)	−138.59703 (0)	−138.54704 (+131.3)	−138.58240 (+38.4)	−138.56628 (+80.7)
UCCSD(T)/cc-pVTZ//UB3LYP/6-311+G(3df)	−138.52412 (+98.3)	−138.54310 (+48.4)	−138.56155 (0)	−138.51149 (+131.4)	−138.54678 (+38.8)	−138.53081 (+80.7)
UCCSD(T)/CBS	−138.58310 (+109.6)	−138.60304 (+57.2)	−138.62483 (0)	−138.57449 (+132.2)	−138.61038 (+29.0)	−138.59406 (+80.8)
UCCSD(T)aug-cc-pVTZ//UX3LYP/cc-pVTZ	−138.53081 (+99.9)	−138.55005 (+49.4)	−138.56887 (0)	−138.51861 (+132.0)	−138.55430 (+38.3)	−138.53818 (+80.6)
UCCSD(T)aug-cc-pVTZ//UBMK/cc-pVTZ	−138.53233 (+101.2)	−138.54997 (+54.9)	−138.57089 (0)	−138.52072 (+131.7)	−138.55492 (+41.9)	−138.53840 (+85.3)

**Table 2** Energies (hartree), relative energies (kJ mol<sup>-1</sup>) and UCCSD(T) CBS limits (hartree) of doublet and quartet linear, kite and fan isomers of C<sub>3</sub>Al

Level of theory	<sup>2</sup> Linear	<sup>4</sup> Linear	<sup>2</sup> Kite	<sup>4</sup> Kite	<sup>2</sup> Fan	<sup>4</sup> Fan
UCCSD(T)/aug-cc-pVDZ//UB3LYP/6-31 + G(d)	-355.75938 (+ 6.5)	-355.71434 (+ 127.3)	-355.76184 (0)	-355.68959 (+ 189.7)	-355.75399 (+ 23.2)	-355.71459 (+ 124.0)
UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df)	-355.86101 (+ 11.7)	-355.81666 (+ 128.3)	-355.86550 (0)	-355.79101 (+ 195.5)	-355.85379 (+ 30.7)	-355.83238 (+ 110.8)
UCCSD(T)/cc-pVQZ//UB3LYP/6-311 + G(3df)	-355.88651 (+ 15.2)	-355.84301 (+ 129.5)	-355.89232 (0)	-355.81673 (+ 198.5)	-355.87906 (+ 34.8)	-355.85117 (+ 108.0)
UCCSD(T)/cc-pVTZ//UB3LYP/6-311 + G(3df)	-355.85358 (+ 11.7)	-355.80831 (+ 130.5)	-355.85803 (0)	-355.78245 (+ 198.4)	-355.84628 (+ 30.9)	-355.81491 (+ 113.2)
UCCSD(T)/CBS	-355.91268 (+ 17.6)	-355.87126 (+ 126.3)	-355.91938 (0)	-355.84496 (+ 195.4)	-355.90526 (+ 37.0)	-355.87160 (+ 125.4)
UCCSD(T)/aug-cc-pVTZ//UX3LYP/cc-pVTZ	-355.86080 (+ 12.2)	-355.81663 (+ 128.2)	-355.86546 (0)	-355.78159 (+ 220.2)	-355.82519 (+ 117.7)	-355.82340 (+ 110.4)
UCCSD(T)/aug-cc-pVTZ//UBMK/cc-pVTZ	-355.86082 (+ 10.1)	-355.81632 (+ 126.9)	-355.86467 (0)	-355.78208 (+ 216.8)	-355.78767 (+ 116.5)	-355.82365 (+ 107.7)

theory are contained in Tables 1 and 2, Fig. 1–8 and Tables S3–S7, ESI†.

Two other levels of theory were also investigated for comparison with the data obtained as outlined above. These were (i) UCCSD(T)/aug-cc-pVDZ//UB3LYP/6-31 + G(d); energy data contained in Tables 1 and 2 and Tables S3–S7 (ESI†), and (ii) UCCSD(T)/cc-pVQZ//UB3LYP/6-311 + G(3df); selected energy data are listed in Tables 1 and 2.

Intersystem crossing data for doublet and quartet C<sub>3</sub>B potential surfaces were obtained at the CASSCF/6-31 + G(d) using a standard method.<sup>72–75</sup> The CAS was selected following the procedure suggested by Anglada and Bofill,<sup>76</sup> based on the fractional occupation of the natural orbitals generated from the first-order density matrix calculated from an initial multi-reference single- and double-excitation configuration interaction wave function correlating all valence electrons. The details of active spaces chosen for the doublet and quartet CCCB involve the  $\sigma$ (CB), the  $\pi$  and the corresponding antibonding orbitals plus the p orbitals on C describing the radical structure. For kite and fan structures C<sub>3</sub>B, the  $\sigma$ (CB), the  $\sigma$ (CC) and the  $\pi$ (CCC) orbitals, and the corresponding antibonding orbitals plus the p orbitals on C or B have been taken into consideration.

Standard enthalpies of formation for all C<sub>3</sub>B and C<sub>3</sub>Al isomers are recorded in Table S10, ESI†.

All calculations were performed with the Gaussian 03 suite of programs<sup>77</sup> using the Aquila supercomputer of the South Australian Partnership for Advanced Computing.

## Results and discussion

### 1. Levels of theory and basis sets used

It has been shown previously that unrestricted density function theory (UDFT) is able to describe radicals and biradicals satisfactorily in many cases.<sup>78–80</sup> In past studies of rearranging CCCX systems, the B3LYP/6-31 + G(d) level of theory has been found adequate to describe geometries, with CCSD(T)/aug-cc-pVDZ//6-31 + G(d) used to determine the relative energies of minima and transition states on these potential surfaces.<sup>7–9</sup> However, previous theoretical studies of C<sub>3</sub>B and C<sub>3</sub>Al stable isomers have shown that (i) doublet and quartet states are involved in these systems<sup>42,56,61</sup> (none of

our previous studies<sup>6–9</sup> have involved ground state quartet structures), and (ii) there is some doubt as to which is the lowest energy isomer in the C<sub>3</sub>Al system using various levels of theory, for example using MP2 or B3LYP with basis sets 6-31G(d), 6-311G(d), cc-pVTZ *et al.*, G1, G2 and QCISD/6-311G(d).<sup>56,61</sup> As a consequence, it is necessary to determine a model appropriate for the present study.

A comparison of the absolute and relative energies of the doublet and quartet structures of the linear, kite and fan isomers of the systems C<sub>3</sub>B and C<sub>3</sub>Al has been carried out using three levels of theory: these data are listed in the first three lines of each of Tables 1 and 2. The first level of theory is that used in previous studies, namely UCCSD(T)/aug-cc-pVDZ//UB3LYP/6-31 + G(d).<sup>7–9</sup> The second level of theory also uses geometry optimization with the spin-unrestricted version of the Becke 3LYP method, but with the split-valence 6-311 + G(3df) basis set (which includes a single diffuse sp shell, triple d-polarization and a single additional f-polarization on carbon, boron and aluminium atoms).<sup>81</sup> Energies have been determined using the UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df) level. The third and highest level of theory considered is UCCSD(T)/cc-pVQZ//UB3LYP/6-311 + G(3df).

The geometries of particular isomers obtained at the three levels of theory are very similar (data not included here), and the trend in relative energies is consistent using the three levels of theory. The comparison of computer time (in hours) using our facility required to complete a structure using the three levels of theory is *ca.* 1–2 : 10–15 : 100–120. The highest level of theory is uneconomic in terms of computer usage, and the intermediate system, [UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df)], was chosen for this study.† This is a higher

† Vibrational frequencies calculated for CCCB geometries measured at the UB3LYP/6-311 + G(3df) level of theory give better values than those given by the UB3LYP/6-31 + G(d) level of theory. Calculated values at the (a) lower and (b) higher levels of theory are, respectively: (i) quartet CCCB: calculated (a) 1566.4 and 2111.3 cm<sup>-1</sup> (b) 1557.5 and 2077.4 cm<sup>-1</sup>; experimental<sup>42</sup> 1512.5 and 2008.2 cm<sup>-1</sup>. To correct the first calculated value needs scaling factors of 0.9710 at the UB3LYP/6-311 + G(3df) and 0.9656 at the UB3LYP/6-31 + G(d) level of theory, making the higher level the better of the two for predicting vibrational frequencies for CCCB.<sup>82</sup> For CCCAl both levels of theory give a calculated vibrational frequency of 1245.0 cm<sup>-1</sup>(15) so the scaling factor (0.9725) is the same for both.

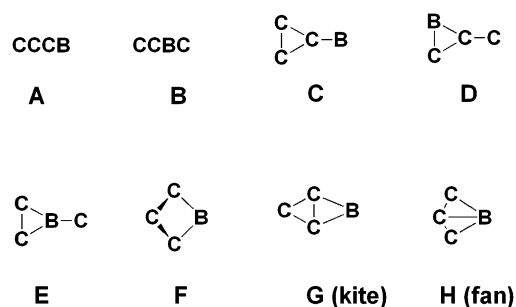
level of theory than those used in previous studies of  $C_3Al$  isomers. All geometries indicated in tables or figures were calculated using UB3LYP/6-311+G(3df), with energies [in hartree (and  $\text{kJ mol}^{-1}$  for relative energies)] using UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311+G(3df). For comparison, reaction coordinate profiles have also been computed at the lower level of theory [UCCSD(T)/aug-cc-pVDZ//UB3LYP/6-31+G(d)]; energies in hartree and relative energies in  $\text{kJ mol}^{-1}$  are listed in Tables S3–S7, ESI† (geometry data determined at this level are not included).§

## 2. The rearrangements of quartet and doublet CCCB: the structures of isomeric $C_3B$ radicals

Essentially we are searching for ways in which the CCCB system can rearrange its backbone to form CCBC. Either, or both of the kite and fan isomers could be formed and either (or both) may be involved in the possible rearrangement of CCCB to yield CCBC in which the carbon atoms may be scrambled. In principle, there are doublet and quartet forms of eight isomers that could be involved in the doublet and quartet CCCB to CCBC rearrangements. These are shown in Scheme 1 and identified by the letters A to H.

The reactions of energized radical CCCB (A) are complicated because CCCB has two forms, a quartet linear CCCB and a bent doublet CCCB (for structures see Fig. 1), with the quartet being the ground state by  $49.8 \text{ kJ mol}^{-1}$  at the UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311+G(3df) level of theory (see Tables S3 and S4, ESI†). Thus both quartet and doublet  $C_3B$  potential surfaces need to be explored in order to probe the chemistry of energized CCCB. The situation is even more complex when the cyclized isomers are considered. The kite and fan isomers G and H (Fig. 1) have stable doublet and quartet structures, but in both cases the doublet is the ground state [by  $131.8$  and  $42.3 \text{ kJ mol}^{-1}$ , respectively (see Tables S3 and S4, ESI†)].

The UB3LYP/6-311+G(3df) geometries of the doublet and quartet forms of the isomers A, G and H are shown in Fig. 1. The structure of linear quartet CCCB shows significant double bond character in the CB bond, while doublet CCCB contains essentially a single CB bond (the bond length of the CB single bond is reported to be  $1.56 \text{ \AA}$ <sup>86</sup>). The doublet and quartet kite structures (G) are similar, as are those of doublet and quartet H. However, structures H show more double bond character



Scheme 1

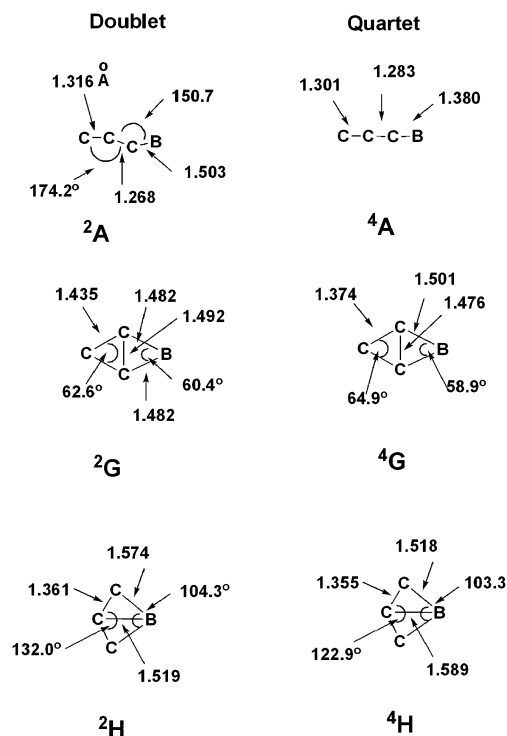


Fig. 1 Selected geometry parameters of doublet and quartet states of isomers linear (A), kite (G) and fan (H) of  $C_3B$  [UB3LYP/6-311+G(3df)].

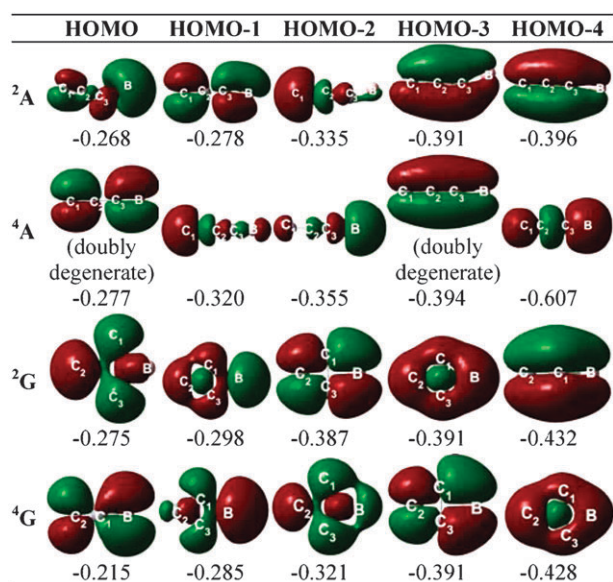
for CC bonds and more single bond character for CB bonds than do structures G.

The valence molecular orbitals of CCCB (A) and kite  $C_3B$  (G) are illustrated in Fig. 2. Quartet CCCB is the ground state since both HOMO and HOMO-3 are doubly degenerate and HOMO-1 is more stable than the corresponding orbital for the doublet state. The energy differences between the LUMO and HOMO of quartet and doublet A are  $5.22 \text{ eV}$  ( $504 \text{ kJ mol}^{-1}$ ) and  $1.80 \text{ eV}$  ( $174 \text{ kJ mol}^{-1}$ ), respectively; thus the quartet state requires more energy to promote an electron. For “rhombus” (kite)  $C_3B$  (G), comparison of the energies of the molecular orbitals for both doublet and quartet indicates that the doublet is the ground state, with the energy differences between LUMO and HOMO being  $3.56 \text{ eV}$  ( $344 \text{ kJ mol}^{-1}$ ) for the doublet and  $3.40 \text{ eV}$  ( $325 \text{ kJ mol}^{-1}$ ) for the quartet.

### 2.1 The rearrangements of quartet CCCB.

The reaction coordinate profiles of the rearrangements of quartet CCCB

§ A reviewer has stated that comparable energies and geometries would be expected using the three B3LYP containing systems. The reviewer suggested that different levels of theory might be tested for the structures listed in Tables 1 and 2 as follows: (i) T to Q extrapolation for yielding the UCCSD(T)/CBS level of theory, and (ii) different hybrid functions of higher level than B3LYP. The levels of theory UCCSD(T)/cc-pVTZ//UB3LYP/6-311+G(3df) and UCCSD(T)/CBS<sup>83</sup> fulfil the first requirement, while the higher level hybrid functions UCCSD(T)/aug-cc-pVTZ//UX3LYP/cc-pVTZ<sup>84</sup> and UCCSD(T)/aug-cc-pVTZ//UBMK/cc-pVTZ<sup>85</sup> fulfil the second requirement. The energies and relative energies resulting from these calculations are recorded in lines 4–8 of Tables 1 and 2, with full details of the higher level hybrid functional calculations given in Tables S8 and S9, ESI†. The geometries of all structures are consistent using the levels of theory described (see *e.g.* Tables S3–S9, ESI†), and relative energies are generally consistent with the exception of the <sup>2</sup>fan  $C_3Al$  structure. We conclude from these data that the level of theory used throughout this paper [UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311+G(3df)] is sufficient to describe the systems under investigation.



**Fig. 2** Shapes and energies (in hartree) of the highest occupied molecular orbitals for the doublet and quartet states for linear and kite  $C_3B$ . UB3LYP/6-311 + G(3df) level of theory.

( $^4A$ ) are shown in Fig. 3 using the UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df) level of theory. Relative energies shown in Fig. 3 are in  $\text{kJ mol}^{-1}$  with reference to  $^4A$  (CCCB) considered as 0  $\text{kJ mol}^{-1}$ . Full details of geometries and energies [UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df) level of theory] of the species shown in Fig. 3 are listed in Table S3 (ESI<sup>†</sup>), which also contains a comparison of energies at the UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df) and UCCSD(T)/aug-cc-pVDZ//UB3LYP/6-31 + G(d) levels of theory for all species shown in Fig. 3.

The overall relative energy from  $^4A$  (CCCB) to  $^4B$  (CCBC) is +82.8  $\text{kJ mol}^{-1}$ . There are two rearrangement processes initiated from  $^4A$ , each of which goes *via* one of the cyclized isomers  $^4G$  and  $^4H$  [respectively, 81.5 and 31.4  $\text{kJ mol}^{-1}$  above  $^4A$  (CCCB)]. Kite and fan isomers are interconvertible over a barrier of 94.6  $\text{kJ mol}^{-1}$  (above  $^4H$ ) [or 126.0  $\text{kJ mol}^{-1}$  (above  $^4A$ )]. Of the two rearrangement profiles, that proceeding *via* fan  $^4H$  is more energetically favourable with a maximum barrier of 184.7  $\text{kJ mol}^{-1}$ , whereas that process which proceeds through kite  $^4G$  requires 253.5  $\text{kJ mol}^{-1}$  of excess energy in order to pass over the final transition state. In this case, although cyclic intermediates  $^4G$  and  $^4H$  may be formed, ring cleavage of these intermediates will reform  $^4A$  (CCCB) rather than giving the rearrangement product  $^4B$  (CCBC).

The rearrangement profiles of  $^4A$  determined at the UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df) and UCCSD(T)/aug-cc-pVDZ//UB3LYP/6-31 + G(d) levels of theory are qualitatively similar. The geometries of minima and transition states are very similar (comparison data not shown), while relative energies are generally within 3–20  $\text{kJ mol}^{-1}$  (see Table S3, ESI<sup>†</sup>).

**2.2 The rearrangement of doublet CCCB.** In spite of the fact that doublet CCCB ( $^2A$ ) lies 49.8  $\text{kJ mol}^{-1}$  higher than the quartet ground state, the rearrangements of  $^2A$  (Fig. 4) are more favourable than those of  $^4A$  (Fig. 3). Full details of

geometries and energies [UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df) level of theory] of the species shown in Fig. 4 are listed in Table S4 (ESI<sup>†</sup>), which also contains a comparison of energies at the UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df) and CCSD(T)/aug-cc-pVDZ//UB3LYP/6-31 + G(d) levels of theory for all species shown in Fig. 4.

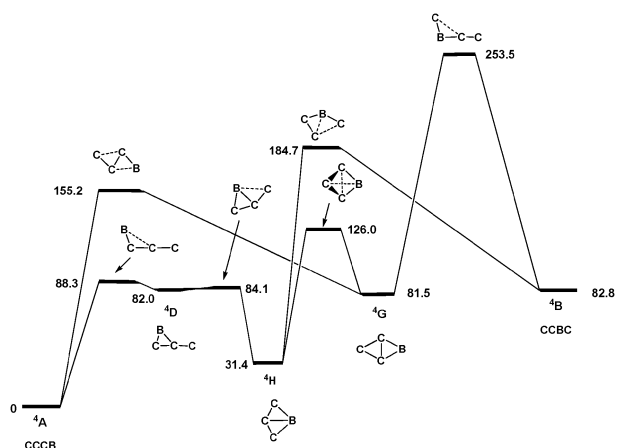
The two reaction coordinates shown in Fig. 4 show differences with those of quartet CCCB (*cf.* Fig. 3). The relative energy for the overall reaction  $^2A$  [considered as 0  $\text{kJ mol}^{-1}$  (see Fig. 4)] to  $^2B$  is only +40.6  $\text{kJ mol}^{-1}$  [*cf.* +82.8  $\text{kJ mol}^{-1}$  (Fig. 3)]. Conversion of  $^2A$  to  $^2B$  may (i) proceed through fan isomer  $^2H$  (−60.7  $\text{kJ mol}^{-1}$ ), (ii) go directly through  $^2G$  (−99.2  $\text{kJ mol}^{-1}$ ), or (iii) go indirectly through  $^2G$  *via*  $^2H$ . All of these rearrangement processes are feasible, and in this system, both cyclic isomers  $^2H$  and  $^2G$  are more stable than  $^2A$ . The reaction profiles shown in Fig. 4 [calculated at UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df)] are qualitatively similar to those calculated at the lower CCSD(T)/aug-cc-pVDZ//6-31 + G(d) level of theory (see Table S4, ESI<sup>†</sup>).<sup>¶||</sup>

**2.3 The possibility of intersystem crossing from  $^4A$  to  $^2A$ .** It has been shown above that even though  $^2A$  is not the ground state species of CCCB, it should rearrange more readily to  $^2B$  (CCBC) than quartet  $^4A$  may interconvert to quartet  $^4B$ . Because the energy difference between doublet and quartet CCCB is only 49.8  $\text{kJ mol}^{-1}$ , the possibility of intersystem crossing of the two states of *A* must be considered. The spin–orbit coupling constant for  $^4A/^2A$  at the CASSCF/6-31 + G(d) level of theory\*\* (CASSCF is contained in the Gaussian 03 package) is 10.4  $\text{cm}^{-1}$ ,

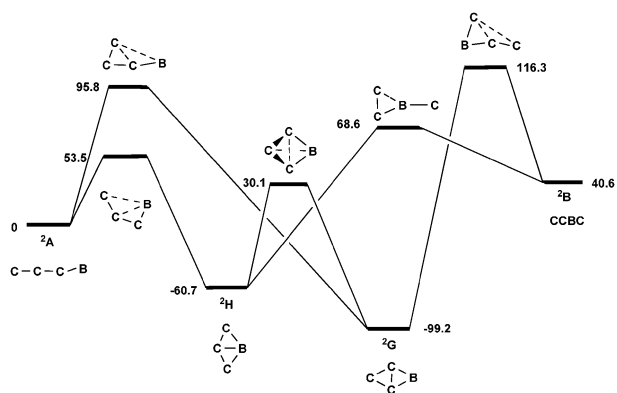
<sup>¶</sup> A reviewer has suggested that the structures of  $C_3B$  (and  $C_3Al$ ) isomers and of their rearrangement mechanisms could be described in terms of the valence bond method so that a reader may visualise mechanisms (as depicted for example in Fig. 3 and 4) in a simple way. For each structure, there are a number of contributing structures to the valence bond resonance hybrid, some showing double bonds and others single bonds and with contributing structures often with electrons at different positions. Such representations are more confusing than simplifying and do not indicate energy states. It is simpler to consider the structures in tables and the reaction profiles in the figures. The structures in the figures do not indicate bond multiplicities, but relative positions of atoms of minima and transition states. Detailed geometries of minima and transition states are recorded in the tables, ESI<sup>†</sup>.

<sup>||</sup> A reviewer has indicated that we should discuss the computed electron densities of atoms for all isomers of  $C_3B$  and  $C_3Al$ . *If we knew the position of the unpaired electron in a doublet structure and those of the three unpaired electrons in the corresponding quartet, such data could assist our understanding of the mechanisms of the rearrangement processes.* Interpretations of calculated electron densities from theoretical data should be used with caution. There are a number of ways to determine atom electron densities using the software available with the Gaussian program. Of these, we chose to use three methods: the Mulliken, NBO and AIM procedures. The data obtained for all structures are included in Tables S11 and S12 (ESI<sup>†</sup>) together with appropriate references. There is no consistency when the three sets of data are compared. All that can be said with certainty is that B and Al are electron deficient and that a particular C atom (or several C atoms) in each structure are electron rich. Some authors choose a sole method to calculate electron density in order to aid explanation of the reactivity of a cumulene (*e.g.* the Mulliken method),<sup>61</sup> whereas others may choose another method (*e.g.* the AIM method).<sup>87</sup>

\*\* Calculation of the spin orbit coupling constant at the higher CASSCF/6-311 + G(3df) level of theory exceeds the memory capacity of the Aquila supercomputer.



**Fig. 3** The reaction coordinate profile of the rearrangement of quartet CCCB. UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df) level of theory. For full details of geometries and energies of minima and transition states see Table S3, ESI†.



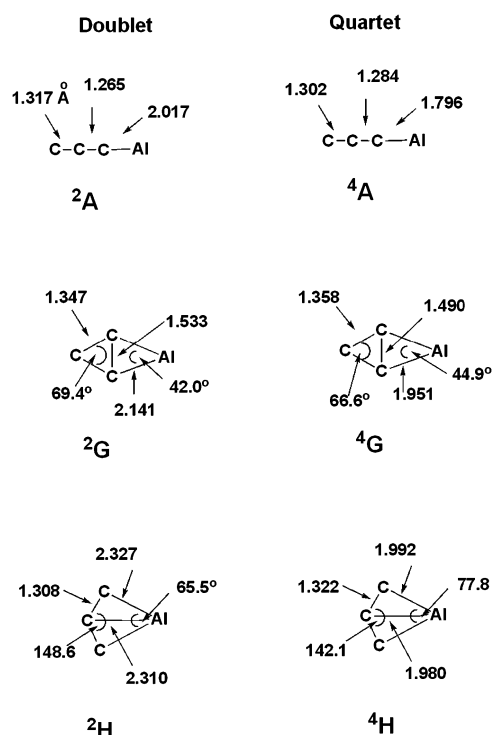
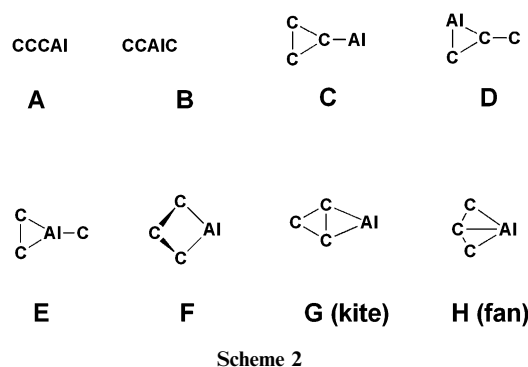
**Fig. 4** The reaction coordinate profile of the rearrangement of doublet CCCB. UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df) level of theory. For full details of geometries and energies of minima and transition states see Table S4, ESI†.

a value large enough to suggest that spin inversion between these two states is possible. This value should be contrasted with the corresponding values for  $^2\text{H}/^4\text{H}$  and  $^2\text{G}/^4\text{G}$  of 3.9 and  $0.3\text{ cm}^{-1}$ , small values indicating that intersystem crossing within these systems should be inefficient.<sup>72–75</sup>

In summary, even though  $^2\text{A}$  is not the ground state species of CCCB, it should rearrange more readily to  $^2\text{B}$  (CCBC) than the corresponding ground state quartet: this process should be favoured by intersystem crossing between  $^4\text{A}$  and  $^2\text{A}$ .

### 3. The rearrangements of doublet and quartet CCCAl: the structures of isomeric $\text{C}_3\text{Al}$ radicals

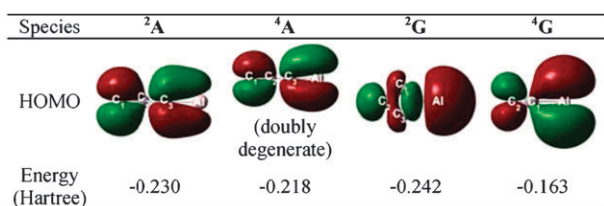
The  $\text{C}_3\text{Al}$  isomers shown in Scheme 2 are identified using the same lettering system adopted for the corresponding  $\text{C}_3\text{B}$  isomers (*cf.* Scheme 1). With the exception of **D** (unstable at the level of theory used in this work), all isomers shown in Scheme 2 are involved in the reaction coordinate profiles of rearrangements of CCCAl. There is some debate as to whether the doublet or quartet states are the ground states of some of



**Fig. 5** Selected geometry parameters of doublet and quartet states of isomers **A**, **G** and **H** of  $\text{C}_3\text{Al}$  [UB3LYP/6-311 + G(3df)].

these isomers. Zheng *et al.* report<sup>61</sup> that the lowest energy isomer is the quartet of **G** [B3LYP/6-311G(d), MP2/6-311G(d)], whereas Barrientos *et al.*<sup>56</sup> consider that the doublets of **A**, **G**, and **H** are the ground states in each case, with the doublet linear species **A** being the lowest energy isomer [MP2(full)/6-311G(d), G1, G2, B3LYP/6-311G(d), CCSD(T)/cc-pVTZ]. Calculations at the UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311 + G(3df) level of theory are in accordance with doublet states being the ground states of **A**, **G** and **H** [by 116.4, 195.6 and  $80.1\text{ kJ mol}^{-1}$ , respectively] (see also Fig. 5). This feature is illustrated by the HOMOs and relative energies of linear CCCAl and kite  $\text{C}_3\text{Al}$  shown in Fig. 6. In this figure it can be seen that the energies favour the doublets as ground states in spite of the doubly degenerate HOMO of quartet CCCAl. The relative stability of the three isomers linear CCCAl ( $^2\text{A}$ ), kite  $\text{C}_3\text{Al}$  ( $^2\text{G}$ ) and fan  $\text{C}_3\text{Al}$  ( $^2\text{H}$ ) are  $^2\text{G}$  ( $0\text{ kJ mol}^{-1}$ )  $>$   $^2\text{A}$  ( $+11.8\text{ kJ mol}^{-1}$ )  $>$   $^2\text{H}$  ( $+30.7\text{ kJ mol}^{-1}$ ) in accordance with the trend reported previously by Barrientos *et al.*<sup>62</sup> In contrast, the other





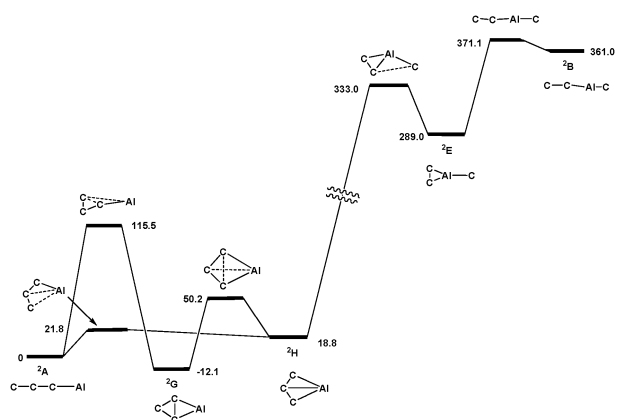
**Fig. 6** Valence molecular (Alpha electrons) orbitals of linear and kite structures of neutral  $C_3Al$  calculated at the UB3LYP/6-311+G(3df) level of theory.

structures shown in Scheme 2 that have stable doublet and quartet states on the rearrangement reaction coordinates, namely CCAIC (**B**) and **E**, have ground state quartets (by 59.6 and 72.8  $\text{kJ mol}^{-1}$ , respectively).

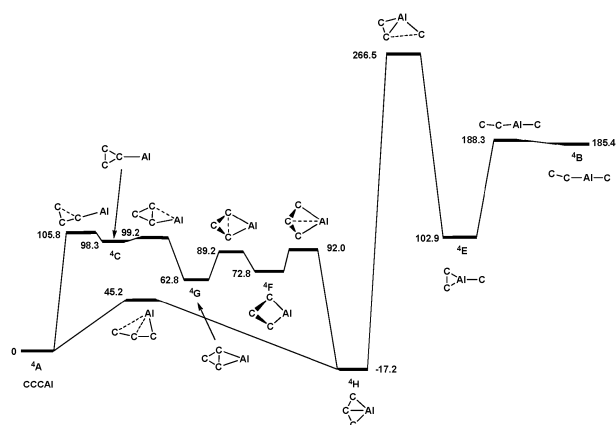
The geometries of the doublet and quartet states of the three key isomers, **A**, **G** and **H**, are shown in Fig. 5. Doublet and quartet CCCAl are linear and the C–Al bond in the ground state doublet has more single bond character than for the quartet (the bond length of the CAI single bond is reported to be 2.24  $\text{\AA}$ <sup>77</sup>). The doublet and quartet kite structures (**G**) are similar, but the doublet shows more single bond character in the central CC bond and the two CAI bonds than the quartet. The geometries of doublet and quartet fan structures **H** are similar, but there is more single bond character for CAI bonds in the doublet.

**3.1 The rearrangements of doublet and quartet CCCAl.** The potential surface for rearrangement of doublet CCCAl ( $^2A$ ) is shown in Fig. 7. Details of geometries and energies of minima and transition states shown in Fig. 7 are contained in Table S5, ESI<sup>†</sup>. Rearrangement to either of the kite or fan isomers ( $^2G$  or  $^2H$ ) is facile, and these two species interconvert over a barrier of only 50.2  $\text{kJ mol}^{-1}$ . In contrast, conversion of  $^2H$  to  $^2B$  (CCAIC) is unfavourable, since there is a barrier of 371.1  $\text{kJ mol}^{-1}$  to the transition state for ring opening of  $^2H$ .

The quartet potential surface (Fig. 8) is more complex. For full details of geometries and energies of minima and transition states shown in Fig. 8 see Tables S6 and S7 (ESI<sup>†</sup>). Quartet CCCAl can rearrange to an essentially equilibrating mixture of



**Fig. 7** The reaction coordinate profile of the rearrangement of doublet CCCAl. UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311+G(3df) level of theory. For full details of geometries and energies of minima and transition states see Table S5, ESI<sup>†</sup>.



**Fig. 8** The reaction coordinate profile of the rearrangement of quartet CCCAl. UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311+G(3df) level of theory. For full details of geometries and energies of minima and transition states see Tables S6 and S7, ESI<sup>†</sup>.

kite  $^4G$  and fan  $^4H$  isomers, *via* non-planar  $^4F$ , with a maximum barrier of 92.0  $\text{kJ mol}^{-1}$ . Conversion of  $^4H$  to  $^4B$  (CCAIC) is not favourable because of the barrier of 266.5  $\text{kJ mol}^{-1}$  required to surmount the transition state in order to effect ring opening of  $^4H$ .

Intersystem crossing between doublet and quartet potential surfaces has not been considered for this system because the energy difference between  $^2A$  and  $^4A$  is 116.4  $\text{kJ mol}^{-1}$ .

In summary, the data shown in Fig. 7 and 8 show that doublet and quartet CCCAl should cyclize to produce kite and fan isomers **G** and **H**, but ring opening of **H** and/or **G** will reform CCCAl rather than effect conversion to CCAIC. Reaction profiles (Fig. 7 and 8) on the doublet and quartet  $C_3Al$  potential surfaces determined at the UCCSD(T)/aug-cc-pVTZ//UB3LYP/6-311+G(3df) are qualitatively similar to those calculated at the lower UCCSD(T)/aug-cc-pVDZ//UB3LYP/6-31+G(d) level of theory (see Tables S5–S7, ESI<sup>†</sup>).

## Conclusions

1. Rearrangements of the quartet (ground state) and doublet forms of CCCB (**A**) to produce CCBC (**B**) proceed through cyclic fan (**G**) and kite (**H**) isomers. Rearrangement is more energetically favourable through the doublet state of CCCB, and intersystem crossing between quartet and doublet CCCB may precede rearrangement of doublet CCCB.

2. Energized doublet (ground state) and quartet CCCAl should undergo facile rearrangements to the two cyclized isomers **G** and **H** (Scheme 2), but bond cleavages of these species to yield CCAIC are energetically unfavourable in comparison to conversion back to CCCAl.

3. Any investigation to probe for the presence of  $C_3B$  and  $C_3Al$  systems in interstellar regions should involve the search for the linear and the two fully cyclized isomers in each system.

4. We have previously used the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31+G(d) level of theory to describe heterocumulene systems (*e.g.* ref. 7), but because  $C_3B$  and  $C_3Al$  include stable quartet structures, we compared calculations at this level with those determined at a number of higher levels of theory.



The study shows that the lower level of theory [UCCSD(T)/aug-cc-pVDZ//UB3LYP/6-31+G(d)] is adequate to define qualitatively both doublet and quartet potential surfaces of C<sub>3</sub>B and C<sub>3</sub>Al.

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