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Ti_8C_{12}: Barrierless Transformation of the T_h Isomer to the T_d Isomer

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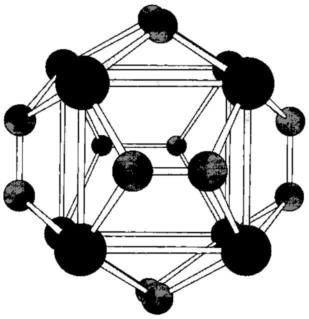
The prototypical metallocarbohedrene Ti_8C_{12} was discovered by Castleman et al. in 1992 and proposed to have a structure, **1**, in which six C_2 groups are bonded over the faces of a Ti_8 cube, parallel to the edges, with symmetry T_h.[1] Subsequently I showed by density functional calculations that an alternative structure, **2**, was very much more stable.[2] Structure **2**, symmetry T_d, is comprised of an inner tetrahedron $(Ti^i)_4$ capped by an outer tetrahedron $(Ti^o)_4$, with the six C_2 groups aligned along the $Ti^o{-}Ti^o$ diagonals of the folded $(Ti^i)_2(Ti^o)_2$ rhombuses over the surface. Theoretical evaluations have encompassed these and other proposed isomeric structures,[3−13] and also congeners containing the other metals Si,[3] Zr,[1c,3b,11,14−17] Hf,[1c,15] V,[1cd,3,16,18,19] Nb,[16,19−22] Cr,[16,23] Mo,[16,23] and Fe,[3b,16,23] but in the absence of pure samples suitable for spectroscopic or diffraction investigation the question of the structure for M_8C_{12} has been approached indirectly. Experimental data on the staging of sequential addition reactions of small molecules to $[M_8C_{12}]^+$ have been interpreted in terms of the types of metal atoms,[18,21,24−27] because in isomer **1** all M atoms are equivalent, while isomer **2** has two sets $(M^i)_4(M^o)_4$. Measured cross-sections for diffusion of $[Ti_8C_{12}]^+$ through inert gas have been interpreted in terms of its structure.[28,29]



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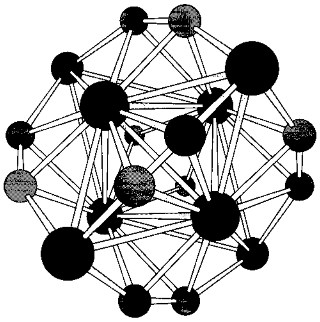

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However, I now show that there is a barrierless pathway from isomer **1** to isomer **2** of Ti_8C_{12}, with the consequence that even metastable occurrence of **1** is not possible.

This result is obtained during optimization of the geometrical structure by minimization of the total energy, following the gradients of the geometry−energy hypersurface. The total energy is calculated by nonlocal density functional (NLDF) methods.[30] Geometrically, the isomer transformation **1** $\Rightarrow$ **2** requires four Ti atoms to move inward along threefold axes to form Ti^i, four to move outward to become Ti^o, and the six (C_2) groups to twist from being parallel to the edges of Ti_4 squares in **1** to being aligned with the long diagonal of folded $(Ti^i)_2(Ti^o)_2$ rhombuses of **2**. The transformation requires intermediate loss of mirror symmetry and ideally can retain symmetry T from T_h to T_d. However isomer **1** of $[Ti_8C_{12}]^0$ as described by NLDF is subject to small Jahn−Teller distortion from the ideal T_h symmetry and is better described in symmetry D_{2h}. Therefore the energy minimization was constrained with lesser symmetry, D_2.

Figure 1 describes the energy and geometry changes during 33 steps of the transformation for Ti_8C_{12}. In steps 1−8 there is a slight energy reduction, but substantial twisting of opposite C_2 groups, and small increases in all of the Ti−Ti distances to allow this twisting. The main energy reduction in steps 10−25 is associated with reduction in the $Ti^i{-}Ti^i$ distances from 4.5 to 3 Å and the formation of 12 new Ti−C lateral bonding contacts which are the major source of the additional stabilization. The final stage, steps 26−33, involves completion of the C−C twist and symmetrization of **2**. The key results are that the geometrical changes are concerted, and at no point does the energy increase. Calculations on $[Ti_8C_{12}]^+$ (the species observed mass spectrometrically) show the same $\mathbf{1}^+ \Rightarrow \mathbf{2}^+$ transformation with a total energy improvement of 301 kcal mol^{-1}.

Changes in the electronic structure of the cluster can also be mapped throughout the transformation. Figure 2 shows the energies of the higher filled bonding orbitals and lower empty orbitals for **1**, for the intermediate at step 20, and for **2**. In **1**

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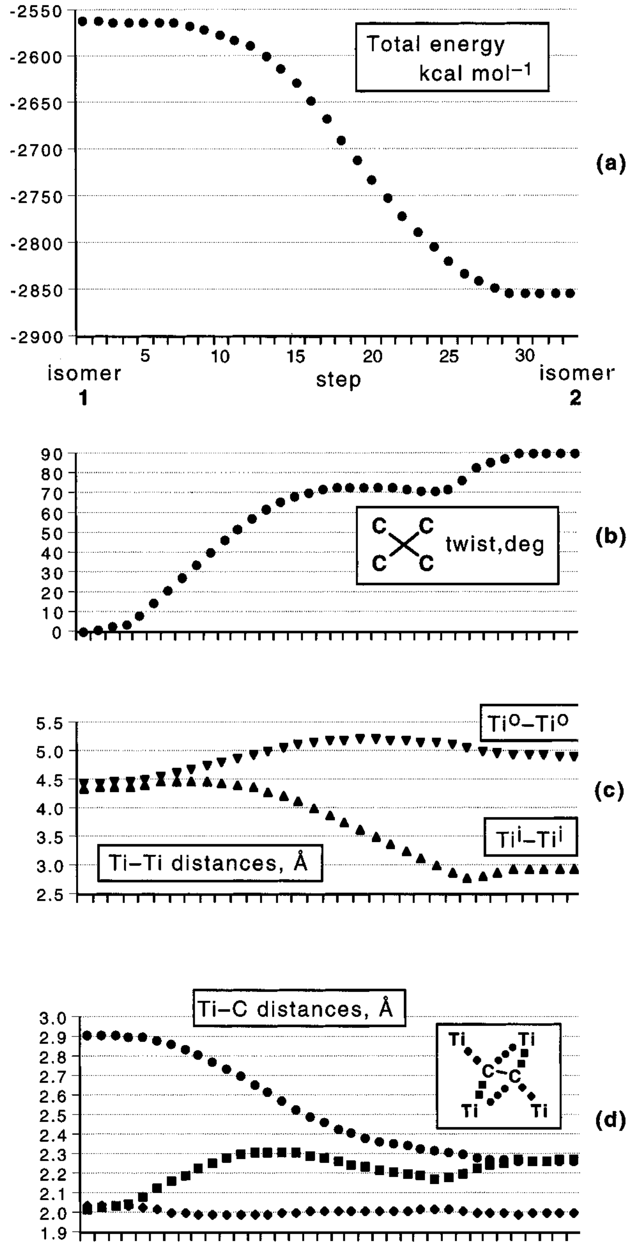

Figure 1. Energy and geometry changes during 33 steps of the transformation of isomer **1** to isomer **2** of Ti_8C_{12}. (a) the binding energy (kcal mol^{-1}); (b) the twist of opposite C_2 groups, expressed as the C−C−C−C torsional angle; (c) the Ti^i−Ti^i and Ti^o−Ti^o distances (Å); (d) the three relevant types of Ti−C distance (Å). Imposed symmetry was D_2: small variations of distances and angles from symmetry T have averaged in this presentation.

there are 20 weakly bonding electrons from −3.5 to −3.0 eV, above a gap of 2.3 eV to bonding orbitals below −6.1 eV, while in **2** there are only two weakly bonding electrons (occupying two sets of almost triply-degenerate orbitals[5b]) with 18 electrons bonding between −4 and −5 eV. The diagram for intermediate 20 shows a broader spread of these occupied orbitals and of the more bonding orbitals down to −11 eV and shows lesser degeneracies corresponding to small variations from symmetry T during the transformation.

A key issue is the shape of the energy surface at structure **1** and the magnitude of any distortion necessary to initiate the transformation. Structure **1** is subject to Jahn−Teller distortion from T_h and has four electrons in the three very closely spaced orbitals at the Fermi level.[31] The starting point for the transformation of $[Ti_8C_{12}]^0$ involved displacement of four Ti atoms only, each by 0.03 Å, which caused an energy increase of only 0.3 kcal mol^{-1}, which is less than ambient thermal energy (and of magnitude similar to the Jahn−Teller stabilization). For $[Ti_8C_{12}]^+$ the initial distortion prior to spontaneous isomerization was again only four Ti atoms each by 0.03 Å, causing an energy increase of 0.5 kcal mol^{-1}. It may be possible to cause isomerization with even smaller initial distortions. However, it is clear that any barrier to isomerization must be less than ambient thermal energy. The conclusion is that the dodecahedral T_h isomer of Ti_8C_{12} cannot exist.

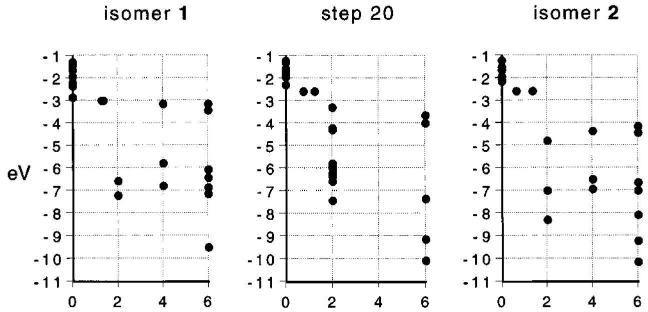

Figure 2. Representation of the energies (eV) and occupancies of higher orbitals for Ti_8C_{12} as isomer **1**, the intermediate at step 20, and isomer **2** (38 more stable filled orbitals in each case are not shown). The horizontal axis gives the number of electrons in each orbital. In these density functional calculations, close-lying states are treated as partly occupied orbitals. For isomer **1** there are three almost degenerate orbitals containing a total of four electrons at −3.0 eV, and 20 electrons (6 + 6 + 4 + 4) between −2.9 and −3.5 eV. For isomer **2** at −2.6 eV there are two close sets of almost triply-degenerate orbitals, containing a total of two electrons, and then a gap to orbitals between −4 and −5 eV containing 18 electrons.

Similar calculations show that addition of one or more ligands (such as NH_3, CH_3CN, or C_2H_4) to **1**, necessarily differentiating the Ti atoms on first addition, also initiates transformation to other isomers.[32] Isomerizations occur also for isomer **1** of $[Zr_8C_{12}]$, $[V_8C_{12}]$, and $[Nb_8C_{12}]$, although the details of any initial barriers are still to be fully investigated: the V−V distances in isomer **1** of $[V_8C_{12}]$ are shorter than those in $[Ti_8C_{12}]$, with the consequence that the initial twisting of C_2 groups requires more expansion of the V_8 cube. Chen et al.[11] previously showed that the T_h isomer of Zr_8C_{12} is not an energy minimum.

The level plateau character of the energy surface of isomer **1** is further demonstrated by its transformations to alternative isomers, particularly the D_{2d} and C_{2v} isomers,[4] with different arrays of diagonal C_2 groups: these alternative transformations are initiated by different starting directions for the energy minimizations. In contrast, transformations between different isomers with diagonal C_2 will have large energy barriers, and of the isomers of M_8C_{12} which contain C_2 groups, it is expected that only the T_h isomer, **1**, would undergo barrierless transformations.

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[31] Isomer **1** was optimized in symmetry D_{2h}, which allowed the Jahn−Teller distortion but prevented the isomerization.