Theoretical Approach to the Synthesis of [2,2,2]Propellane

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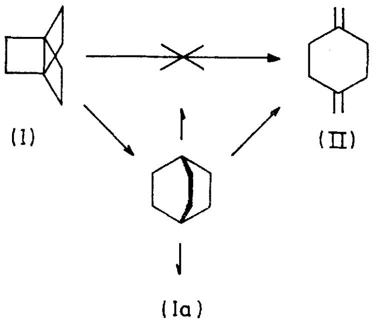
Summary INDO calculations indicate that the triplet state of dimethylenecyclohexane should rearrange to geometrically relaxed triplets which should collapse preferentially to the ground state, [2,2,2]propellane.

The propellanes have been the subject of much recent synthetic[1] and theoretical[2,3] interest. In particular, [2,2,2]propellane (I), as yet unprepared, poses unique theoretical and synthetic problems. The instability introduced by increasingly directing the bonding electrons of the bridgehead carbons towards one hemisphere might be offset by that induced by decreasing the bridgehead C–C–C angles below 90°. Thus the relative length of the C–C bonds in compound (I) remains a subject of some conjecture.

Table *Comparison of optimized geometries for the singlet states and triplet states of* [2,2,2]*propellane. Bond lengths are in* Å. *In ref.* 3 *only the* C(1)–C(4) *bond was varied.*

	Singlet				Triplet
	(I)		(Ia)		
Bond	This work	Ref. 3	This work	Ref. 3	This work
C(1)–C(2)	1·500	—	1·470	—	1·480
C(2)–C(3)	1·500	—	1·500	—	1·490
C(1)–C(4)	1·515	1·52	2·290	2·54	1·928
C–H	1·120	—	1·130	—	1·130

Although compound (I) should not rearrange to dimethylenecyclohexane (II) by a thermal 2 + 2 retroaddition since such a process is symmetry forbidden, compound (II) has been observed in unsuccessful attempts to synthesize (I).[4] Hoffmann[2] has shown that compound (I) can rearrange to (II) *via* intermediate (Ia), which represents a second minima on the potential surface for the ground state of [2,2,2]propellane. The second minima owes its existence to the crossing of the highest occupied and lowest unoccupied MOs (which have opposite symmetry with respect to the plane bisecting the C_{3v} axis) as the distance between the bridgehead carbons increases. Newton and Schulman[3] have calculated the relative stabilities of both (I) and (Ia), as well as the barrier between them using *ab initio* methods and 2 × 2 configuration interaction. Their calculations suggest that compound (I) should be sufficiently stable to be characterized.



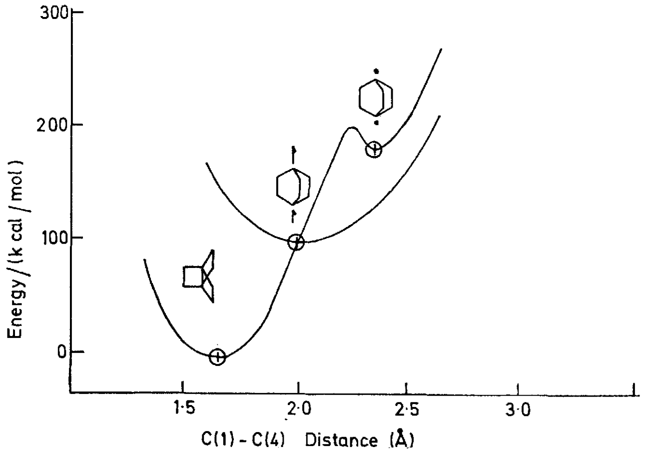


Figure. *Plot of energy* vs. *central bond length for the lowest singlet and triplet state of* [2,2,2]*propellane. Circled points represent optimized geometries. Other bond lengths vary slightly* (*see Table*).

We have performed INDO calculations on the lowest triplet state as well as both conformations of the lowest singlet state of [2,2,2]propellane. The geometries were optimized for all bond lengths and C–C–C bond angles. A C_{3v} axis of symmetry and a mirror plane bisecting this axis were assumed. The tetrahedral angle of 109·47° was used for all H–C–H angles. The geometries summarized in the Table were shown to be optimized as any change in any of the variables increased the energy. One should interpret the INDO relative energies (I) and (Ia) with caution as the closely related CNDO approximation has been reported to overestimate the stability of isomers containing small rings.[4] Also, the absence of configuration interaction might increase the calculated energies of the single states, particularly in the region of the surface where the two MOs cross. Nevertheless, the Figure illustrates that the optimum geometry for the triplet state has a distance intermediate between that of (I) and (Ia). Furthermore, the calculations suggest that vertical relaxation of the optimized triplet might form a ground-state configuration that would preferentially collapse to (I) rather than (Ia).

The triplet state of dimethylenecyclohexane (II) should rearrange to geometrically relaxed triplets which should collapse preferentially to the ground state (I). Photochemical population of the triplet of (II) thus indicates a synthetic approach to [2,2,2]propellane.

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