A Comment on the Mechanism of Enantiotopomerization of Tetrahedral Boron Chelates; Model MNDO Calculations

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The experimentally observed enantiotopomerization of diarylboron salicylideneaminato-chelates (1) are indicated by model MNDO calculations not to proceed *via* planar tetraco-ordinate boron transition states (2), but rather by ring opening–ring closure mechanisms.

Detailed theoretical studies of planar tetraco-ordinate forms involving main group elements[1,2] are now inspiring experimental investigations.[3,4] Although normal tetrahedral geometries are preferred energetically, generally by large amounts, appropriate substituents may stabilise the planar forms sufficiently to permit experimental detection.[1]

Minkin's group has just reported a study of the enantiotopomerization of diarylboron salicylideneaminato-chelates (1).[3] A planar tetraco-ordinate boron transition state (2) was postulated. Instead, we suggest a rather trivial mechanistic alternative, ring opening to (3) combined with rotation around the O–B bond and reclosure.

We have examined Minkin's system by means of MNDO calculations on the simplified models, (4)—(7). MNDO, the most reliable and general semiempirical LCAO–SCF method, has been tested widely and should be adequate for this purpose.[5] The initial state model (4) was found to have a classical structure (details are shown in the structural formula), and a rather low heat of formation, −207.1 kJ/mol. A planar structure corresponding to (5) was submitted, but the

geometry-optimisation routines inherent in the MNDO program led automatically to B–N bond rupture and ring opening. Structure (6) [ΔH_f(MNDO) = −81.0 kJ/mol] was obtained by imposing C_s symmetry. No stationary point with a planar (or slightly pyramidal) tetraco-ordinate boron could be located on the potential energy surface. To simulate the reaction pathway, the B–N distance was lengthened sequentially and no other symmetry constraints imposed. Various twisted open forms resulted with heats of formation in the −90 to −110 kJ/mol range. A planar *s-trans* structure (7), ΔH_f(MNDO) = −113.9 kJ/mol was a second minimum. While we have not located the transition state for an enantiotopomerization

(4),C_s

Minimum

(5),C_s

(6),C_s

Planar restricted

(7),C_s

Minimum

(1)

(2)

(3)
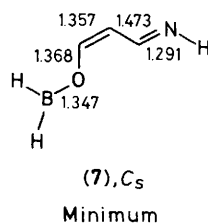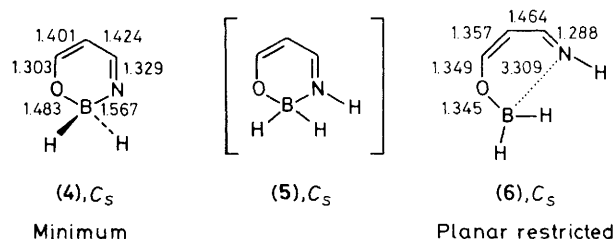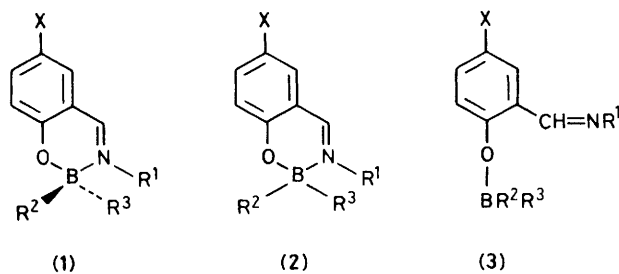
explicitly, its energy probably is similar. We note that the calculated energy difference between (4) and (7), 93 kJ/mol, agrees quite well with the activation energies for (1) found experimentally. The experimental activation entropies (mostly 23—36 J mol^{-1} K^{-1})[3] seem more in accord with a ring-opened transition state than with a process involving simple rotation around the boron centre.

Our model calculations on (4)—(7) involve hydrogen substituents on boron. In the experimental system (1), the R^2 and R^3 substituents are much more bulky aryl groups. Steric factors alone make structures like (2) unlikely. Our calculations indicate that B–N bonding in such hypothetical planar arrangements also is unfavourable energetically.

As we have shown in similar[1,2] and in other contexts,[6] it is desirable to test mechanistic and structural proposals with readily available and easily applied theoretical calculational methods. Like (5) [and (2)], we have examined many planar tetraco-ordinate candidates by calculations, but have found them to prefer classical structures with lower co-ordination instead. Cumulene perimeter systems[2] and planar phenonium ions[7] afford examples.

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