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THE PREFERRED CONFORMATION OF BICYCLO[3,3,2]DECANE

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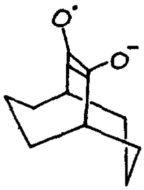
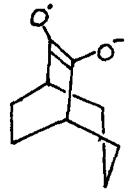
The preferred conformations (1) and (2) have been assigned[2] to bicyclo[3,3,2]decane-9,10-semidione and bicyclo[3,2,2]nonan-6,7-semidione, on the basis of e.s.r. hyperfine splitting constants. Extrapolation of this data led to the proposal that bicyclo[3,3,2]decane itself preferred the boat-chair[3] conformation (3(b)). However, the transposition of the conformational preferences of flexible molecular segments from ring system to ring system without consideration of the molecule in question as a whole can often lead to erroneous conclusions.

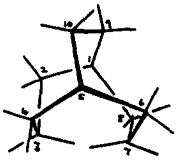


(1)

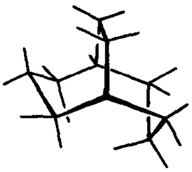


(2)

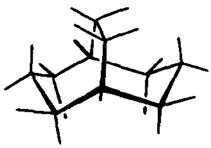
The solution infra-red spectra of certain bicyclo(3,3,2)decane derivatives exhibit the high frequency ν(CH) and δ(CH) absorption bands usually associated with interaction between two or more methylene groups in close proximity[4]. Such abnormally high absorption bands must be associated with transannular methylene interactions between C-3,C-7 in conformation (3a), or between C-3, C-9(or C-10) in conformations (3b) and (3c); or between C-2, C-6 (or C-4, C-8) in conformation 3(d).



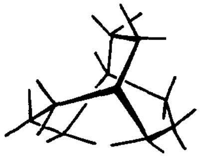
3a



3b



3c



3d

We have now investigated the δ(CH) bands of a number of such compounds.

Bicyclo(3,3,2)decane and the corresponding 9-alcohol, 9-acetate[5] and 9-ketone exhibit bands at 1484; 2982 and 1483, 1486; and 1470 cm^{-1} respectively whereas no such abnormal absorptions are detectable for the 2-olefin[5], 3-ketone[5,6] or 2-ene-9[5] and 2-ene-10-ketone[5]. Further, the 9,10-diketone[5], and evenmore significantly, 9-oxabicyclo[3,3,3]decane-10-one[7] show maxima at 1485; 2994 and 1489 cm^{-1}, *thus supporting the view that these high frequency bands arise from methylene-methylene interactions between C-3 and C-7 in the twin-chair conformation (3a) or between C-2 and C-6(or C-4 and (C-8) in the twin twist-boat conformer (3d*

In this context[2] it is notable that the 9-olefin exhibits no abnormal δ(C-H) absorption, though the *bis*-trimethylsilylether of bicyclo[3,3,2]dec-9-ene-9,10-diol[5] shows maxima at 2990 and 1489 cm^{-1}. Thus, the boat-chair conformation (3b) seems to be preferred only in those bicyclo[3,3,2]decane derivatives which are forced to adopt a fully eclipsed arrangement about C-9 and C-10 (viz. the semidione and 9-olefin) (unless there are other steric factors mitigating against this conformation, as in the *bis*-trimethylsilylether described), whereas these compounds which can adopt a C-9; C-10 staggered arrangement seem to prefer a twin-chair (or twin twist-boat) conformation. In support of this statement, it is worth noting that the ultra-violet spectrum of bicyclo(3,3,2)-9,10-dione has λ_{max}(EtOH) 421 nm. which according to Leonard and Mader[8] indicates a small but definite stagger between C-9 and C-10.

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