facile pathway for electron transmission consistent with the lower limit of the rate constant. In PNBPA, on the other hand, the strongly electrophilic nitro group serves as a trap for the attacking or transferred electron so that electron transmission into the metal center is considerably slower. The reaction of e_{aq}^- with aromatic nitro compounds shows the effect of electron localization of the NO_2 group[15] with the pK_a for the protonation–deprotonation of these radicals having values of 2.2–3.9.[16]

These results are of relevance to electron-transfer processes involving external reducing agents.[17] However, it is premature at this time to attempt to account for the behavior of PNBPA when reduced by Cr(II)[18] on the basis of the observations reported here involving much simpler one-electron reducing agents.

Acknowledgment. We thank Dr. E. Hayon for his interest in this work and for making the pulse radiolysis apparatus available to us.

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(15) K. D. Asmus, A. Wigger, and A. Henglein, *Ber. Bunsenges. Phys. Chem.*, 70, 862 (1966).

(16) W. Grünbein, A. Fojtic, and A. Henglein, *Z. Naturforsch., B*, 24, 1336 (1969).

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(18) E. S. Gould, *J. Amer. Chem. Soc.*, 88, 2987 (1966).

(19) (a) Boston University; (b) University of Texas; the encouragement of Professor E. L. Powers is appreciated.

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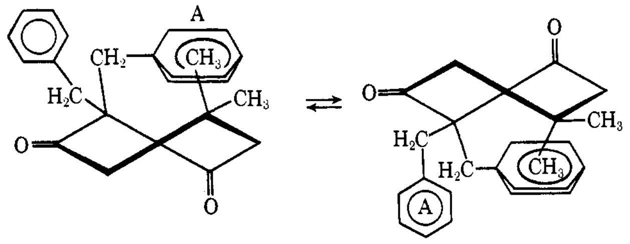
Experimental Demonstration of the Relative Flexibility of Boat and Chair Forms of the Cyclohexane Ring

Sir:

It is generally recognized that eclipsing interactions are diminished in the boat forms of cyclohexanones, and, as a result, a number of cases of monocyclic alkyl-substituted cyclohexanones existing nearly exclusively in a twist-boat conformation have been identified.[1] The latter is often called the flexible form, a reference to the mechanical mobility of ball and stick models which can be easily distorted and interconverted among the variety of possible conformations. In contrast, the chair cyclohexane is designated as the rigid form because of the mechanical resistance experienced in conformational transformations of the models.[2,3] However, actual differences in mobility of the boat and chair forms have never been demonstrated[4] experimentally, *i.e.*, by any direct measurement of *molecular* rather than model energy parameters. Thus, it has always been a matter of interest as to whether the mechanical properties of the model in any way reflect factors inherent in the molecular structure to which analogy is presumed.

We now present direct evidence of the greater mobility of the boat as compared to the chair form gathered in studies of the pmr spectra of 1,1-dimethyl-4,4-dibenzylcyclohexane (**1**) and its derivatives. In view of earlier observations[1] and generalizations[2] (cited above) we can confidently anticipate that the 3,5-diketone **2** would manifest all the features of the boat form. Thus, its pmr shows only three sharp singlets, aside from the phenyl multiplet grouping centered on *ca.* 430.2 Hz. These singlets are structurally correlated in Table I. Precisely the same spectrum is seen at temperatures below −80°. This suggests that low temperatures do not freeze out any important modes or seriously interfere with the flexibility, hence interconvertibility, of the boat conformations.

In support of this conclusion is the unusually high field of the methyl singlet, 19.5 Hz, which is to be identified with conformations of **2** bringing the respective methyl groups within the shielding cones of the transannular benzene rings in rapid alteration. Only an extremely flexible motion sweeping the groups attached at the bowsprit (1,4) positions back and forth could accommodate these pmr characteristics of the twist-boat conformation of **2**. Furthermore, this mobility of boat–boat interconversions persists at temperatures far below that required to observe slowing (half-peak separation, −66.7°)[3] of the rate of chair–chair interconversions.



2

On the other hand, the parent molecule **1**, which in the boat form is characterized by serious eclipsing interactions among the substituents of the cyclohexane ring, would be expected to prefer the chair conformation. The pmr of **1** clearly reveals it to be in an exceedingly rigid chair even at ambient temperatures (see Table I). It exhibits two widely separated, sharp, methyl singlets corresponding to very different environments of these groups, which, apparently, are very resistant to interconversion. Furthermore, neither of these methyl singlets is unusually shielded, in keeping with chair conformations in which the shielding cones of the transannular benzene rings are far removed from influencing the methyl resonances. Moreever, there are also to be noted two distinct benzylic methylene absorptions, which are indicative of a lack of mobility in conformational interconversions, and quite different than was demonstrated (above) for the twist-boat **2**. Finally, we note in the spectrum of **1** the broad band of unresolved multiplets ranging from 92 to 44 Hz. These comprise the absorptions of the

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(1) See, for examples, N. L. Allinger and H. M. Blatter, *J. Amer. Chem. Soc.*, 83, 994 (1961), and C. Djerassi, E. J. Warawa, J. M. Berdahl, and E. J. Eisenbraun, *ibid.*, 83, 3334 (1961).

(2) For a discussion of these terms, see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962, p 204 *et seq.*, and P. Hazebroek and L. J. Oosterhoff, *Discuss. Faraday Soc.*, 10, 87 (1951).

(3) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Amer. Chem. Soc.*, 84, 386 (1962).

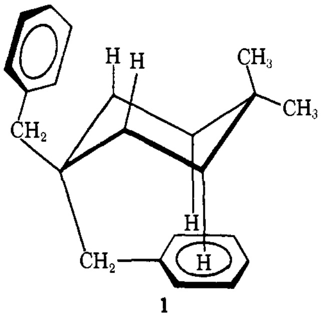
(4) Possible indirect demonstrations of the flexibility of the twist-boat conformation could be deduced from various data reported by: (a) N. L. Allinger and L. A. Freiberg, *J. Amer. Chem. Soc.*, 82, 2393 (1960); (b) E. W. Garbisch and D. B. Patterson, *ibid.*, 85, 3228 (1963); and (c) H. Booth and G. C. Gidley, *Tetrahedron Lett.*, 1449 (1964).

Table I. Pmr Data[a]

Structure	Signal Position, Hz	Approx wt	Multiplicity	Assignment
1	430	10	Narrow unresolved band	Phenyl
	157 151	2 each	Singlet[b]	Benzylic methylene
	92–44	8	Complex multiplet	Ring methylene
	62.5 57	3 each	Singlet[c]	Methyl
2	430.2	10	Narrow unresolved band	Phenyl
	190.5	4	Singlet	Benzylic methylene
	118	4	Singlet	Ring methylene
	19.5	6	Singlet	Methyl

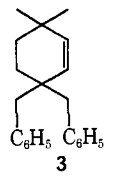
[a] $CDCl_3$ solvent, TMS standard. [b] These singlets show definite indications of complex, unresolved splitting. [c] Sharp line showing no indications of multiplicity.

eight ring methylene protons. The complexity of this pattern and the somewhat shielded positions of these absorptions (*cf.* the ring methylene peak of **2** at 118 Hz) suggest two significant inferences. These protons are rigidly fixed in axial or equatorial positions, unlike the case[3] of cyclohexane itself which is experiencing rapid chair–chair interconversions averaging into a single sharp line at 85.2 Hz. In addition, their higher field positions compared to the cyclohexane singlet are indicative of influence by the shielding cone of the transannular benzene rings, in what appears to be the most attractive way of representing the immobile chair conformation of **1**.



1

The purity of **1** has been rigorously tested by all accepted glc standards. Its structure is confirmed by the pmr (Table I), the cmr (eight lines, exclusive of aromatic ring, grouped in the saturated carbon region:[5] δ ^{13}C from C_6H_6, 96.31, 94.16, 86.93, 86.07, 83.86, 83.37, 80.08, 79.30 ppm), mass spectrum (M^+ 292, principal peaks *m/e* 201, 105, and 97, and base peak 91), and its synthesis by hydrogenation of **3**, which in turn was formed from **2** *via* steps of reduction and dehydration without rearrangement, as attested by the pmr and cmr. Moreover, the cmr spectrum completely verifies the rigidity of the ring since it establishes beyond cavil[5] the doubling of methyl and benzylic methylene carbon resonances. Further proof of the structure and rigidity of **1** rests on a comparison of properties, including (220 MHz) pmr and (Fourier transform) cmr, with an analog **4** whose rigidity is enforced by the fusion of a three-membered ring in its bicyclic structure. Neither **1** nor **4** shows any coalescence of axial and equatorial protons in the pmr at temperatures >150°. To our knowledge there are no known cyclohexanes which show a barrier to chair–chair interconversions even approaching this magnitude (>20 kcal). An understanding of the interaction mechanism giving rise to this highly unusual property is certainly required.



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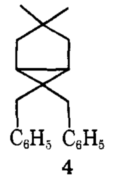

4

One possibility is that the severely hindered rotation of the axial benzyl group in **1** must be coupled with the flipping of the ring. This can be perceived by considering the general conformer concept of Ugi, *et al.*,[6] which anticipates such circumstances. This treatment expresses positional exchange processes of molecules with flexible skeletons in terms of subclasses of conjugate elements of a group S_n, where n here refers to the number of skeleton positions in a conformer. The various subclasses associated with mechanism have to be assigned to different types of barrier situations. In the case of **1**, flipping of the ring involved in chair–chair interconversions corresponds to a different subclass than the combination of six-membered ring flipping and rotation of methyl or benzyl groups. If rotation of the benzyl group is suppressed by a high barrier, it automatically leads to suppression of the last named type of mechanism.

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[5] D. K. Dalling and D. M. Grant, *J. Amer. Chem. Soc.*, **89**, 6612 (1967).

[6] Private communication with Professor I. Ugi; one of us (H. K.) is particularly grateful to Professor Ugi for the benefit of a prepublication copy of an article discussing this approach; see P. Gillespie, P. Hoffman, H. Klusachek, D. Marquarding, S. Pfohl, F. Ramirez, E. A. Tsolis, and I. Ugi, *Angew. Chem., Int. Ed. Engl.*, **10**, 687 (1971).