ethyl trifluoroacetate[42] (-38 cal deg^{-1} mole^{-1}) and ethyl trichloroacetate[43] (-43 cal deg^{-1} mole^{-1}). The transition states for these reactions should have appreciable charges located on oxygens bound to the former carbonyl carbon,[40] yet the variation in the value of $\Delta S°$ for generating such charges in the corresponding acids is not reflected in $\Delta S^{\ddagger}$. Whether this results from dominance of the entire solvent structure around the transition state by those features required to produce this very negative $\Delta S^{\ddagger}$,[40] from nonequilibrium solvation of the transition state,[44] or from other factors remains unanswered.

Acknowledgment. This work was supported in part by grants (GP-4422 and GP-7488) from the National Science Foundation.

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Kinetic Study of Ring Inversion in 9,10-Disubstituted *cis*-$\Delta^{2,6}$-Hexalins, [4.4.4]Propella-3,8,12-triene, and 3,3-Difluoro[4.4.4]propellane

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Abstract: The kinetic parameters for ring interconversions were measured in three hexalin (I–III) and two propellane derivatives (IV, V). Measurements were performed by the comparison of the calculated and experimental nmr spectra line shapes at various temperatures. The results indicate two characteristic reaction paths, applicable to saturated and unsaturated compounds, respectively. It is suggested that in the saturated compounds the reaction profile has discrete steps involving one ring at a time. On the other hand in the unsaturated compounds the reaction profile seems to contain only one maximum.

The kinetics of the chair–chair interconversion have been studied both experimentally and theoretically in cyclohexane and its derivatives.[1–5]

The ring interconversions have also been studied in *cis*-decalins and substituted *cis*-decalins.[6–9] On the basis of the experimental results and theoretical calculations, an energy profile containing four minima has been suggested for this interconversion.[6,8] The following stepwise mechanism has been assumed. (a) Conversion of a chair into a twist-boat in one ring, with an activation energy close to that of the cyclohexane inversion. This implicitly assumes that the presence of the second ring has a small effect on the conformational change. (b) The second ring undergoes a chair to twist-boat transition with the same activation energy as in step a. (c) Both rings undergo a transition to a new twist-boat conformation related geometrically to the final chair–chair conformation. (d) Repetition of steps b and a give the final chair–chair conformation. The major difficulty in confirming this mechanism lies in the fact that experiment provides the over-all energy change but not values for each step. A logical extension of these systems is [4.4.4]propellane which consists of three condensed saturated rings. In this study we report measurements on the ring interconversions in this system.

Ring interconversion has also been studied in cyclohexene[3,10] and in a substituted cyclohexene.[11] The measured free energy of activation, $\Delta G^{\ddagger}$, for cyclohexene is 5.3 kcal/mole.[10] Beckett, *et al.*,[12] have theoretically derived the value of 2.7 kcal/mole for the difference between the half-chair and boat forms of cyclohexene. By comparing the calculated and experimental results Anet and Haq[10] concluded that the interconversion process in cyclohexene has a similar reaction profile to that of cyclohexane, *i.e.*, that the energy has a minimum in the transition state. Bucourt and Hainaut[3] opposed this view and claimed that not all of the relevant factors had been taken into account by Beckett, *et al.* In a more elaborate calculation, these authors have obtained a value of 6.9 kcal/mole for the energy difference between the boat and half-chair forms in cyclohexene. They have also calculated the energy involved in other steps of the half-chair–half-chair interconversion and concluded that an energy minimum is absent in the neighborhood of the transition state portion of the reaction profile. This presumably shows that the interconversion mechanism in cyclohexene is substantially different from that in cyclohexane, the latter having a minimum

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(12) C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *ibid.*, **70**, 4227 (1948).

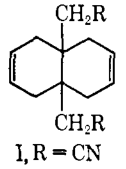
Table I. Nmr Parameters and Kinetic Data for 9,10-Disubstituted *cis*-Hexalins

R	J_{AB},[c] cps	δ_{AB},[c] ppm	E,[a] kcal/mole	Log k_0[a]	$\Delta S^{\ddagger}$,[b] eu	$\Delta G^{\ddagger}$,[b] kcal/mole
Br	10.0 ± 0.2	0.215 ± 0.008	13.7 ± 0.8	13.9 ± 0.5	2.9	12.2
CN	16.3 ± 0.2	0.388 ± 0.008	12.6 ± 1.6	12.5 ± 1.7	−3.3	13.4
CO_2CH_3	12.4 ± 0.2	0.323 ± 0.008	11.4 ± 1.7	10.7 ± 1.8	−11.4	14.2

[a] Arrhenius parameters. [b] Activation parameters calculated at 300°K (J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, New York, N. Y., 1963, p 71). [c] 213°K.

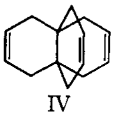
in the energy profile. A study of ring interconversion in hexalins and propellatriene (the two- and three-membered ring analogs to cyclohexene) which is reported here could assist in elucidating more details of the reaction profile of these systems.

The activation energies for interconversion were measured for the compounds I–III. The methylene protons

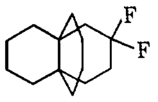


I, R = CN
II, R = Br
III, R = CO_2CH_3

of the angular substituents show a spectrum of the AB type consisting of four resonances when the interconversion rate is slow. At fast rates the spectrum collapses into a singlet. The procedure of interpretation of the spectra in terms of rate constants is identical with that used for 9,10-substituted *cis*-decalins.[7] Also studied were [4.4.4]propella-3,8,12-triene (IV) and 3,3-difluoro[4.4.4]propellane (V). In IV the spectrum is of the



IV



V

AA′BB′XX′ type. The resonances of the allylic protons have been considered to approximate an AB system and the kinetic data were obtained from the changes in its line shape. The ^{19}F nmr spectrum of V is an AB type. It consists of four lines at low temperature and coalesces to a singlet with increasing temperature. Kinetic data were obtained from the changes in the line shapes of the AB-type spectra.

Experimental Section

Materials. Compounds I–IV were available in this laboratory.[13,14] Compound V was prepared as follows. Into a 10-ml Teflon tube placed within an autoclave was placed [4.4.4]propellan-3-one[14] (618 mg), methylene chloride (2.5 ml), and water (0.3 ml). The autoclave was evacuated (water pump) and cooled in a bath of Dry Ice–acetone. Sulfur tetrafluoride (4.5 g, Matheson) was then condensed into the autoclave. Rocking was maintained for 15 hr at room temperature, then the reaction mixture was vented, poured into water (5 ml), and extracted with ethyl ether, and the extract washed with water until neutral. The solvent was removed and the residue was distilled (0.1 mm) at a bath temperature of 120°. The distillate solidified, mp 81–82° (from aqueous ethanol) (310 mg, 44%). *Anal.* Calcd for $C_{14}H_{22}F_2$: C, 73.62; H, 9.73; F, 16.64; mol wt, 228.33. Found: C, 73.54; H, 9.61; F, 17.1; mol wt, 228.

Compounds I–III were dissolved in deuteriochloroform and compounds IV–V in carbon tetrachloride (sealed tubes). Concentrations were about 10% by weight except for V where the concentration was about three times greater.

Spectrometer. Proton spectra were taken on a Varian A60 nmr spectrometer equipped with a V-6040 variable-temperature unit. Fluorine spectra were taken on a Varian DP60 spectrometer operating at 56.4 MHz.

Kinetic analysis was achieved by the comparison of calculated[15] and experimentally determined line shapes. In the high-temperature range we used the approximate formula for fast exchange. In compounds I, III, IV, and V the chemical shift and spin–spin coupling have been measured down to about 30° below the temperature where exchange effects could be observed. No significant changes were detected. This experiment could not be performed on II because of the rather low temperature at which the coalesce of lines started. Therefore in all our calculations we assumed that the chemical shift and the spin–spin interaction are independent of temperature.

Results and Discussion

In the forthcoming discussion it is implicitly assumed that the solvent effects on $\Delta G^{\ddagger}$ are small. The limited number of systems studied so far do not permit a real verification of this assumption. However, the results quoted so far seem to indicate that our assumption is justified.[8,9]

Hexalins (I–III). The chemical shifts (δ_{AB}) and the spin–spin coupling constants (J_{AB}) of the AB systems for compounds I–III at low temperatures are given in Table I. In II the AB resonances are well separated from the rest of the spectrum throughout the entire temperature range studied. In I and III, the upper resonance of the AB quadruplet is obscured by the resonance of the allylic protons. This, however, does not seriously interfere with kinetic interpretation because J_{AB}, δ_{AB}, and the kinetic data could nevertheless be obtained from the remaining three lines. At higher temperature the coalesced AB single resonance is well separated. The plots of log $1/\tau$, where τ is the mean lifetime of the conformer, *vs.* the reciprocal of the absolute temperature, $1/T$, are shown in Figure 1. The activation parameters and Arrhenius constants are given in Table I.

For purposes of comparison of our results with those of others we use $\Delta G^{\ddagger}$ since it has been pointed out that its value in nmr measurements is less sensitive to various experimental inaccuracies.[4,16] Our $\Delta G^{\ddagger}$ values for hexalins are about twice those observed and calculated for cyclohexene.[3,10] This is in accordance with a reaction scheme which assumes that the boat form is of highest energy[3] in the conformational sequence and which requires both rings to invert *simultaneously*. This concerted inversion is due to the rigidity of the hexalin system as is also evident from the examination of models. In the boat–boat form of hexalins the dihedral angle between the 9,10 substituents is zero, which implies that when one ring is in the boat form the other

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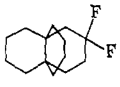
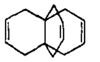
(13) J. Altman, E. Babad, J. Itzchaki, and D. Ginsburg, *Tetrahedron Suppl.*, **8**, Part 1, 279 (1966).

(14) J. Altman, E. Babad, J. Pucknat, N. Reshef, and D. Ginsburg, *Tetrahedron*, **24**, 975 (1968).

(15) S. Alexander, *J. Chem. Phys.*, **37**, 967 (1962).

(16) J. E. Anderson, *Quart. Rev.* (London), **19**, 426 (1965).

Table II. Nmr Parameters and Kinetic Data for Propellanes

Compound	J_{AB}, cps	δ_{AB}, ppm	E_a,[a] kcal/mole	Log k_0[a]	$\Delta S^{\ddagger}$,[b] eu	$\Delta G^{\ddagger}$,[b] kcal/mole
	240 ± 3[c]	4.4 ± 0.1[c]	15.7 ± 0.3	12.8 ± 0.6	−2	15.7
	15.6 ± 0.2	0.97 ± 0.01	16.4 ± 0.4	12.6 ± 0.3	−3	16.7

[a] See footnote *a*, Table I. [b] See footnote *b*, Table I. [c] 261°K.

ring *must* also be in the boat form. This situation is in contrast to that observed in *cis*-decalin where each ring assumes the conformation of highest energy independently of the other. Consequently $\Delta G^{\ddagger}$ for *cis*-decalin does not differ much from that observed for cyclohexane.

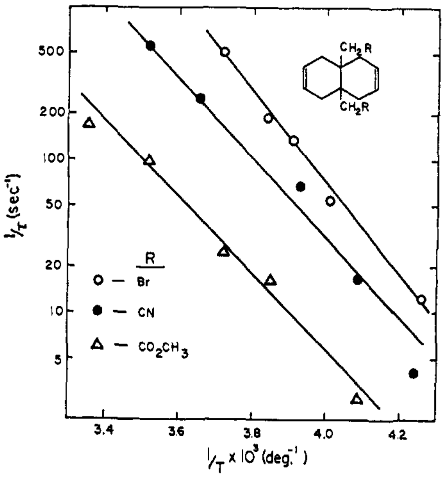


Figure 1. Arrhenius plots for three 9,10-disubstituted *cis*-$\Delta^{2,6}$-hexalins.

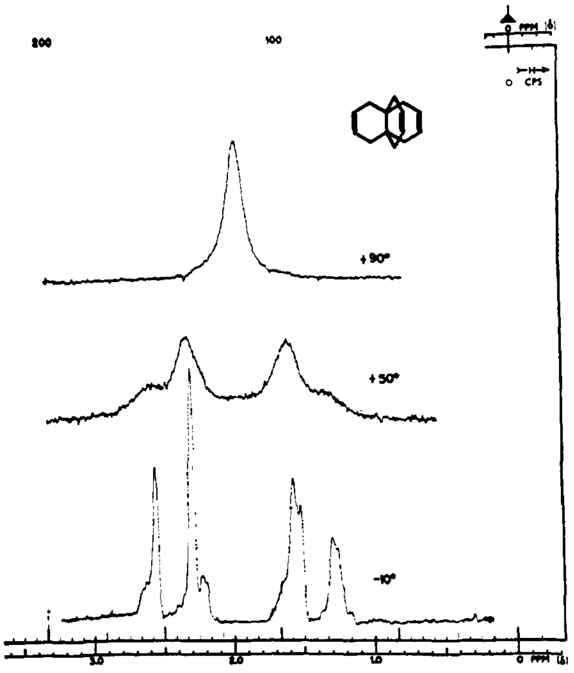


Figure 2. The nmr spectrum of the allylic ring protons in [4.4.4]-propella-3,8,12-triene at various temperatures.

Next, we should consider the effect of the angular substituents on $\Delta G^{\ddagger}$. Although this appears to be small in both hexalin and *cis*-decalin derivatives, it may be of the order of 1–2 kcal/mole, and higher experimental precision would be required to carry out a significant comparison of the parent hydrocarbons and their derivatives.

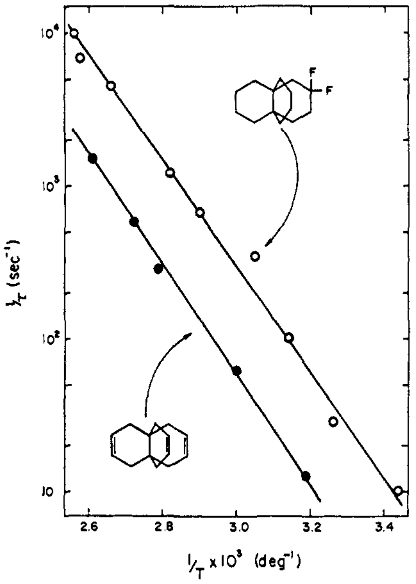


Figure 3. Arrhenius plots for propellanes.

[4.4.4]Propella-3,8,12-triene (IV). The spectrum of the allylic protons of IV is shown in Figure 2. When the vinylic protons are irradiated the small splitting in the upper field half of the quadruplet disappears. Still the presence of several additional small resonances, which are *not* due to impurities, may be observed. This indicates that the spectrum is of the AA′BB′ type. Low-temperature (−80°) and 100-MHz measurements[17] support this assignment. In the low-temperature region the small additional lines were ignored and the kinetic analysis was based on the sharp low-field doublet of the "AB" spectrum. After coalescence the interaction with the vinylic protons was taken into account by superposing two calculated lines with a separation equal to $J_{BX}/2$. Clearly these approximations have introduced some uncertainty in the results. The plot of the reciprocal mean lifetimes *vs.* $1/T$ is given in Figure 3; the calculated parameters are summarized in Table II which also includes the nmr parameters of IV.

[17] We thank Dr. M. Rabinovitz of the Hebrew University, Jerusalem, and Dr. B. Z. Fuchs of Tel-Aviv University for measurements at 100 MHz.

The value of $\Delta G^{\ddagger}$ for IV (Table II) is about three times larger than that obtained for cyclohexene and about one and one-half times that obtained for the hexalins (I–III, Table I). This strongly supports the conclusion reached in the case of the hexalins, *i.e.*, that in unsaturated systems the rings do not interconvert independently. This also implies one maximum in the reaction energy profile. Thus, the interconversion in IV, just as in I–III, is simultaneous for all three rings.

3,3-Difluoro[4.4.4]propellane (V). The spectra of [4.4.4]propellane,[14] which are given in Figure 4, change with temperature indicating the occurrence of a kinetic process. However, their complexity renders interpretation in kinetic terms difficult. This led us to introduce fluorine substitution, a method which has also been used by Gerig and Roberts[8] for *cis*-decalins. The ^{19}F resonance exhibits a simple AB pattern which is easy to interpret. The F–H interaction was not observed, possibly because of the relative broad F resonances (20 Hz for the low-field half of the AB spectrum and 40 Hz for the upper field half of the AB spectrum). The kinetic results and the nmr parameters are given in Figure 3 and in Table II.

It will be noted that $\Delta G^{\ddagger}$ is similar to that obtained for the 9,10-disubstituted *cis*-decalins[7] and differs slightly from the value of unsubstituted *cis*-decalin.[8] It appears that the Gerig and Roberts model discussed above and applied to *cis*-decalins[8] also applies to the *saturated* propellane. The essential feature of this mechanism is the independence of each ring assuming its highest energy conformation within the reaction profile.

Finally it must be emphasized that although the kinetic parameters of IV and V are quite similar, the reaction profile, as discussed above, is most probably quite different.[18]

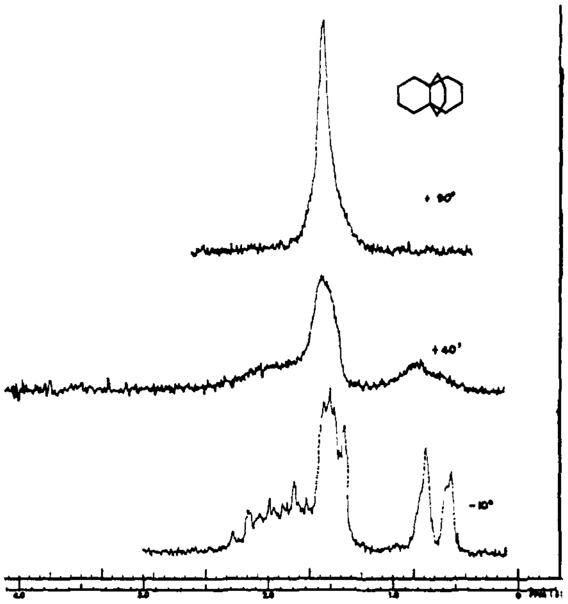


Figure 4. Nmr spectra of [4.4.4]propellane dissolved in carbon tetrachloride at various temperatures.

Acknowledgment. We are indebted to Professor D. Ginsburg for his encouragement and helpful discussions.

[18] Note Added in Proof. Allinger, *et al.* (N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *J. Am. Chem. Soc.*, **90**, 5773 (1968)), have calculated 4.33 kcal/mole for the difference in energy between the boat and the half-chair forms of cyclohexene. They derive a reaction profile similar to that of Anet and Haq[10] and obtain an activation energy of 5.93 kcal/mole.