

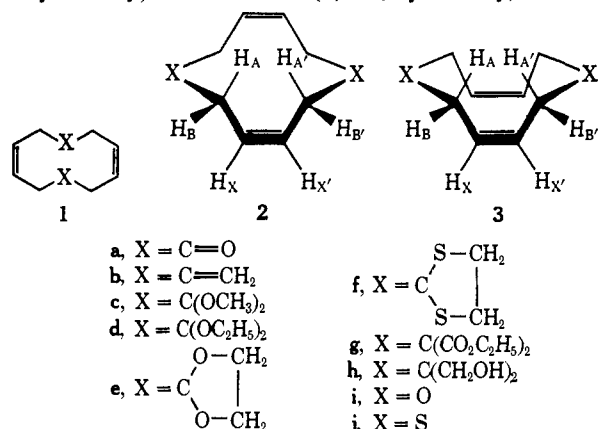
Conformational Mobility in *cis,cis*-1,6-CyclodecadienesBryan W. Roberts,*^{1a} John J. Vollmer,^{1b,2} and Kenneth L. Servis^{1b,3}

Contribution from the Departments of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania 19174, and the University of Southern California, Los Angeles, California 90007. Received December 4, 1973

Abstract: The conformational properties of a series of *cis,cis*-1,6-cyclodecadienes possessing substituents at C-4 and C-9 (**1a–h**) have been studied by proton magnetic resonance spectroscopy. Observation of $A_2XX'A_2'$ and $ABXX'B'A'$ spectra for each compound at the upper and lower temperature limits studied is consistent with ring inversion of a predominant conformer, either the chair (**2**) or the boat (**3**). The absorption pattern of protons external to the ten-membered ring at the slow exchange limit suggested predominance of the chair but was generally equivocal. However, the nonequivalence of exocyclic methylene protons in tetraol **1h** demonstrated a preference for the chair which is probably a general feature of the ring system. Activation parameters for ring inversion were obtained by line-shape analysis of splitting patterns resulting from double irradiation of olefinic protons as a function of temperature. The results reveal a substituent effect on free energies of activation which increase in the order

$C=O < C=CH_2 < \overline{COCH_2CH_2O} \approx C(CH_2OH)_2 < \overline{CSCH_2CH_2S} < C(OCH_3)_2 < C(OCH_2CH_3)_2 < C(CO_2CH_2CH_3)_2$. Inversion probably involves a chair–boat–chair itinerary *via* double bond flipping through a transition state in which positions 4 and 9 have approached each other through pseudorotation. On the basis of this and other studies, the substituent effect appears to be associated with rotational barriers around $-CH_2-X-$ bonds, transannular nonbonding interactions of atoms or groups at positions 4 and 9, and possibly variation of bond angles at positions 4 and 9.

Cyclodeca-1,6-dienes of the *cis,cis* type belong to a family of cyclic dienes, with diametric olefinic bonds of the same geometry connected by odd polymethylene chains, which have been predicted to be capable of existing in strain-free conformations.⁴ Molecular models reveal two important conformations for **1**, the chair (**2**, C_{2h} symmetry) and the boat (**3**, C_{2v} symmetry). When



perfectly staggered, the two conformers are devoid of bond angle strain and differ primarily in the nature of the nonbonded interactions of olefinic bonds and allylic hydrogens. Grob and Schiess⁵ and Dale⁴ have suggested that the chair is preferred because the olefinic bonds and abutting allylic hydrogens ($H_A, H_{A'}$, **2**) just make van der Waals contact whereas in the boat the short distance between double bonds gives rise to a strong repulsive interaction. This strain can be relieved by spreading the double bonds apart, but not without engendering torsional and other sources of strain.

(1) (a) University of Pennsylvania; (b) University of Southern California.

(2) National Science Foundation Cooperative Fellow, 1965–1967; Stauffer Fellow, 1967–1968.

(3) Alfred P. Sloan Research Fellow, 1969–1971.

(4) (a) J. Dale and C. Moussebois, *J. Chem. Soc. C*, 264 (1966); (b) J. Dale, *Angew. Chem., Int. Ed. Engl.*, **5**, 1000 (1966).

(5) (a) C. A. Grob and P. W. Schiess, *Helv. Chim. Acta*, **43**, 1546 (1960); (b) *ibid.*, **47**, 558 (1964).

During the past few years there has been a number of studies to test these premises. These include variable temperature proton magnetic resonance (pmr) studies of the hydrocarbon and various derivatives,⁶ an X-ray crystallographic examination of the 4,9-diketone (**1a**),⁷ an electron diffraction study of the hydrocarbon,⁸ and recent force field calculations on the hydrocarbon⁹ and diketone (**1a**).^{9a} In this paper we present full details of our preliminary report^{6a} on a study by pmr spectroscopy of the dynamic behavior of a series of *cis,cis*-1,6-cyclodecadienes substituted at C-4 and C-9.

Results

The *cis,cis*-1,6-cyclodecadienes examined in this study were prepared by two general routes. In one sequence diketone **1a** was prepared by a modification of Grob and Schiess' procedure^{5a} and converted by a Wittig reaction to the volatile, crystalline tetraene **1b** and by conventional procedures to ketal and thioketal derivatives **1c–f**. In the other sequence, tetraester **1g**^{10a,b} was reduced to tetraol **1h** with lithium aluminum hydride.^{10c}

The 100-MHz ambient temperature pmr spectra of **1a–h** revealed two types of spectral behavior which are exemplified by the spectra of diketal **1e** and diketone **1a**. The spectrum of **1e** in chloroform, aside from an

(6) (a) B. W. Roberts, J. J. Vollmer, and K. L. Servis, *J. Amer. Chem. Soc.*, **90**, 5264 (1968). An account of this work was presented at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Abstract ORGN-142. (b) J. Dale, T. Ekeland, and J. Schaug, *Chem. Commun.*, 1477 (1968). (c) A. Feigenbaum and J. Lehn, *Bull. Soc. Chim. Fr.*, 3724 (1969).

(7) (a) H. L. Carrell, B. W. Roberts, J. Donohue, and J. J. Vollmer, *J. Amer. Chem. Soc.*, **90**, 5263 (1968). (b) An X-ray study of the mercuric chloride complex of the 4,9-dithioether **1j** has also been carried out: K. K. Cheung and G. A. Sim, *J. Chem. Soc.*, 5988 (1965).

(8) A. Almenningen, G. G. Jacobsen, and H. M. Seip, *Acta Chem. Scand.*, **23**, 1495 (1969).

(9) (a) N. L. Allinger, M. T. Tribble, and J. T. Sprague, *J. Org. Chem.*, **37**, 2423 (1972); (b) O. Ermer and S. Lifson, *J. Amer. Chem. Soc.*, **95**, 4121 (1973).

(10) (a) K. C. Murdock and R. B. Angier, *J. Org. Chem.*, **27**, 2395 (1962); (b) R. M. Gipson, H. W. Guin, S. H. Simenson, C. G. Skinner, and W. Shive, *J. Amer. Chem. Soc.*, **88**, 5366 (1966); (c) R. M. Gipson, Ph.D. Dissertation, University of Texas, Austin, 1965.

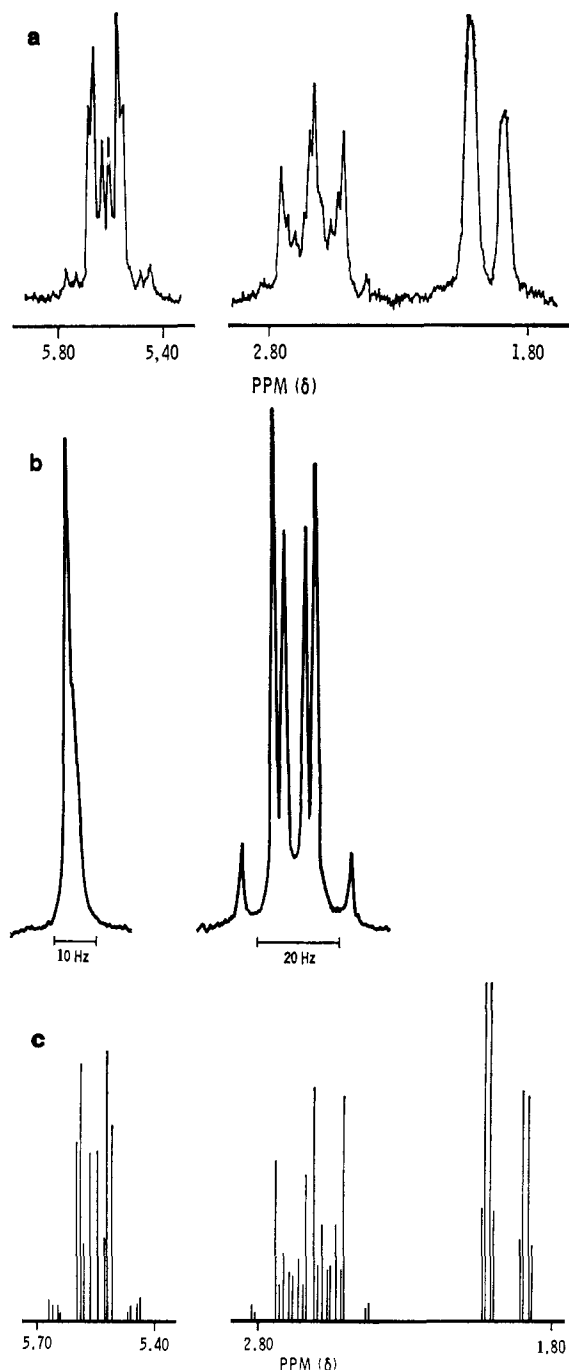


Figure 1. (a) The vinyl and allylic regions of the 100-MHz pmr spectrum of diketal **1e** in $\text{CHCl}_3\text{-CDCl}_3$ at ambient temperature. (b) Vinyl region of **1e** after spin-decoupling from allyl multiplets at 1.96 and 2.63 ppm, respectively. (c) Calculated spectrum of **1e** based on chemical shifts and coupling constant in Tables I and II.

eight-proton singlet at δ 3.98, exhibited a spin-spin splitting pattern of the $\text{ABXX}'\text{B}'\text{A}'$ type (Figure 1a) as expected for a static (on the pmr time scale) *cis*-2-butene fragment as shown in structures **2** and **3**. For this derivative the chemical shift difference $\Delta\nu_{\text{AB}}$ was large enough to permit selective decoupling of all three types of protons. Thus, double irradiation of olefinic protons at δ 5.60 led to collapse of allylic proton absorption to an AB quartet ($\Delta\nu_{\text{AB}} = 67.0$ Hz, $J_{\text{AB}} = 12.9$ Hz), while sequential double irradiation of low field and high field allylic protons led to collapse of the olefinic multiplet to a broad singlet and symmetrical six-line pattern, respectively (Figure 1b). The latter

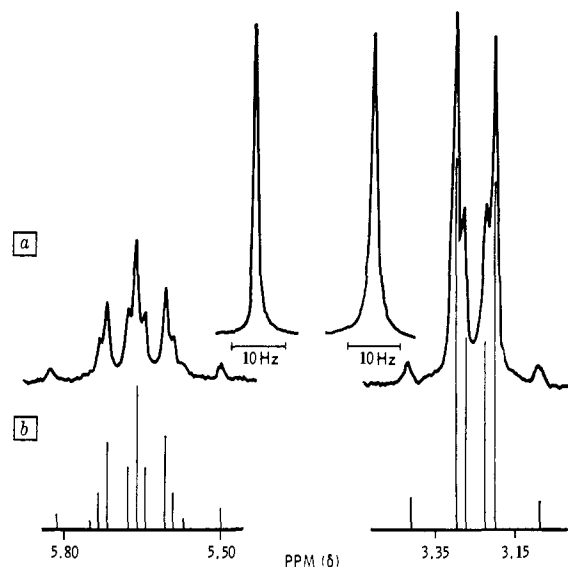


Figure 2. (a) The 100-MHz pmr spectrum of diketone **1a** in $\text{CHCl}_3\text{-CDCl}_3$ at ambient temperature. The offset singlets are spin-decoupled vinyl and allylic multiplets, respectively. (b) Calculated spectrum of **1a** based on chemical shifts from Table II and coupling constants cited in the text.

multiplet was analyzed as the A(X) part of an $\text{AA}'\text{XX}'$ spectrum with negligible homoallylic coupling¹¹ by the Harris method¹³ to give the following coupling constants:¹⁴ $J_{\text{XX}'} = +10.9$ Hz, $J_{\text{AX}} = +11.1$ Hz, and $J_{\text{AX}'} = -0.7$ Hz. According to the empirical relationships (eq 1-4) developed by Garbisch for the di-

$$J_{\text{=CHCH}} = 6.6 \cos^2 \phi + 2.6 \sin^2 \phi \quad (0^\circ \leq \phi \leq 90^\circ) \quad (1)$$

$$J_{\text{=CHCH}} = 11.6 \cos^2 \phi + 2.6 \sin^2 \phi \quad (90^\circ \leq \phi \leq 180^\circ) \quad (2)$$

$$J_{\text{HC=CCH}} = 6.6 \cos^2 \phi - 2.6 \sin^2 \phi \quad (0^\circ \leq \phi \leq 90^\circ) \quad (3)$$

$$J_{\text{HC=CCH}} = -2.6 \sin^2 \phi \quad (90^\circ \leq \phi \leq 180^\circ) \quad (4)$$

hedral angular dependence (ϕ) of three-bond and four-bond allylic-olefinic coupling¹⁵ J_{AX} and $J_{\text{AX}'}$ correlate best with the 11.1- and -0.7 -Hz couplings, respectively. These assignments further establish that the upfield and downfield allylic absorptions arise from H_B and H_A , respectively, in **2** or **3**. Reconstruction of the entire $\text{ABXX}'\text{B}'\text{A}'$ spectrum by computer simulation (Figure 1c) led to coupling constants in excellent agreement with values obtained from spin-decoupled spectra and by calculation from eq 1-4 (Table I). The value of J_{BX} obtained in this fashion correlates well with that calculated from eq 1 with $\phi \cong 60^\circ$.

In contrast to **1e**, diketone **1a** exhibited an ambient temperature 100-MHz spectrum in chloroform of the $\text{A}_2\text{XX}'\text{A}_2'$ type (Figure 2a), which is consonant with a

(11) That this was a reasonable assumption was indicated by (a) the presence of only six of the ten theoretical lines expected if $J_{\text{AA}'}$ ($J_{\text{XX}'}$) is zero,¹² (b) the lack of secondary splitting in the spin-decoupled AB quartet, and (c) computer simulations of undecoupled and decoupled spectra which show that homoallylic coupling as small as 0.5 Hz produces discernible deviations of calculated from experimental spectra.

(12) J. W. Emsly, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Oxford, 1965, pp 392 ff.

(13) (a) R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964); (b) R. K. Harris and C. M. Woodman, *Mol. Phys.*, **10**, 437 (1965).

(14) Signs are based on results of computer simulation of the undecoupled spectrum in which geminal allylic coupling was assumed negative.

(15) E. W. Garbisch, *J. Amer. Chem. Soc.*, **86**, 5561 (1964).

Table I. Coupling Constants (Hz) for **1e** and **1f**

Compd	Method	J_{AB}^a	J_{AX}	$J_{AX'}$	J_{BX}	$J_{BX'}$	$J_{XX'}$	$J_{AB'}, J_{AA'}, J_{BB'}$
1e	Calcd (ϕ) ^b		+11.6 (180°)	0.0 (180°)	+3.6 (60°)	-1.6 (60°)		
	Spin decoupling	-12.9	+11.1	-0.7			+10.9	
	Computer simulation ^c	-12.9	+11.0	-0.7	+3.5	-1.5	+10.9	0.0 ^d
1f	Calcd (ϕ) ^b		+11.6 (180°)	0.0 (180°)	+3.6 (60°)	-1.6 (60°)		
	Spin decoupling	-13.4	+10.8	-0.8			+11.0	
	Computer simulation ^c	-13.4	+10.8	-0.8	+3.5	-1.5	+11.0	0.0 ^d

^a Sign assumed. ^b Calculated from the Garbisch equations, ref 15. ^c ± 0.5 Hz. ^d Assumed.

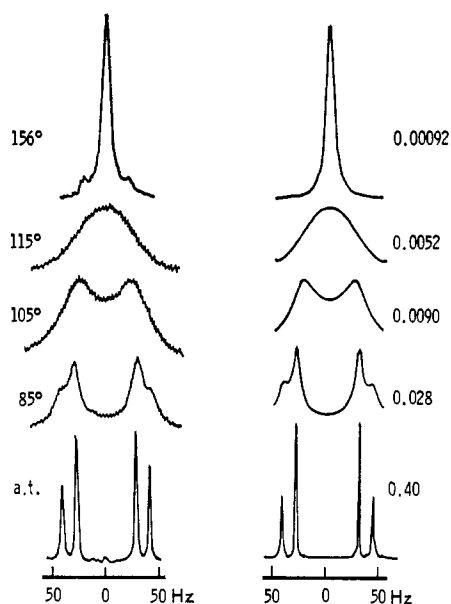


Figure 3. Experimental (left) and calculated (right) spectra of diketal **1e** showing the spin-decoupled allyl region at various temperatures. Each of the calculated spectra is labeled with the appropriate mean lifetime (τ) in seconds.

cis-2-butene fragment in a rapidly inverting ring. Double irradiation of vinyl or allylic protons led to collapse of the other to a sharp singlet (Figure 2a). Computer simulation of the full spectrum (Figure 2b) led to the following constants:¹⁶ $J_{AA} = -12.0$ Hz, $J_{AX} = +8.4$ Hz, $J_{AX'} = -1.3$ Hz, and $J_{XX'} = +10.5$ Hz.

At ambient temperature the spectral behavior of the remaining derivatives paralleled that of **1a** and **1e** depending upon the nature of X. Thus, trigonal derivatives **1a** and **b** and tetrahedral derivatives **1c-h** exhibited well-defined $A_2XX'A_2'$ and $ABXX'B'A'$ splitting patterns, respectively. Each of these collapsed to a singlet and an AB quartet, respectively, upon double irradiation of olefinic protons. Pertinent spectral data are included in Table II. Only in dithioketal **1f** was $\Delta\nu_{AB}$ large enough to permit separate decoupling of allylic protons and analysis analogous to that carried out with **1e**. The results are included in Table I.

Examination of the temperature dependence of spin-decoupled allylic absorption confirmed that the aforementioned $ABXX'B'A'$ and $A_2XX'A_2'$ spectra cor-

(16) The same assumptions regarding signs of coupling constants¹⁴ and homoallylic coupling apply here also. Specifically, the negligible size of homoallylic coupling is indicated by the lack of splitting of the four small inner and outer lines of the allylic multiplet in Figure 2a^{13b} and the noticeable effect of trial values as small as 0.5 Hz on the simulated spectrum.

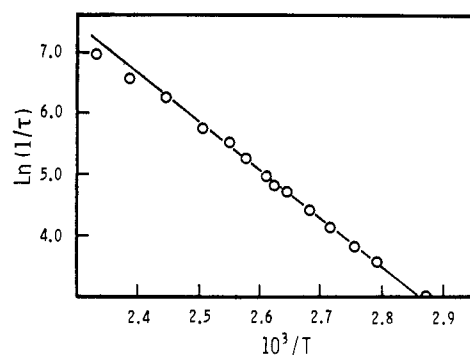
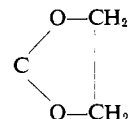
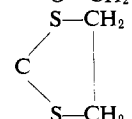


Figure 4. Arrhenius plot of $\ln 1/\tau$ vs. $10^3 T^{-1}$ for diketal **1e**.

respond to slow and fast exchange limits for ring inversion. The spectral behavior of diketal **1e** is typical (Figure 3). Progressive increase of sample temperature

Table II. Ambient Temperature Chemical Shift Data for **1a-h** in $CHCl_3$ - $CDCl_3$

X	δ_{CH_2}	δ_{-CH}	δ_{-X-}
C=O	3.21	5.65	
C=CH ₂	2.77	5.28	4.77 (bs, $W_h = 3.0$ Hz)
	1.96, 2.63	5.60	3.98 (s, $W_h = 1.0$ Hz)
	2.28, 2.91	5.61	3.30 (s, $W_h = 1.0$ Hz)
C(CH ₂ OH) ₂ ^a	1.44, 1.61	5.23	2.95, 3.15, 4.14 ^b
C(OCH ₃) ₂	2.21, 2.37	5.42	3.19 (s, $W_h = 1.0$ Hz)
C(OCH ₂ CH ₃) ₂	2.19, 2.39	5.50	1.26 (t, $J = 7.0$ Hz) 3.60 (q, $J = 7.0$ Hz)
C(CO ₂ CH ₂ CH ₃) ₂	2.49, 2.71	5.25	1.23 (t, $J = 7.0$ Hz) 4.17 (q, $J = 7.0$ Hz)

^a Spectrum recorded in DMSO- d_6 because of limited solubility.
^b ABX spectrum, $J_{AB} = -10.6$ Hz, $J_{AX} = J_{BX} = 5.3$ Hz.

lead to broadening of the AB quartet at $\sim 70^\circ$, coalescence at 115° , and the formation of a singlet at 150° . At the latter temperature, the undecoupled spectrum was essentially identical with that of **1a** at ambient temperature. Quantitative line-shape analysis by visual

Table III. Activation Parameters for Allylic Proton Exchange in **1a-h**

Compd	Solvent	$\Delta\nu_{AB}$, Hz	J_{AB} , Hz ^a	$\Delta G^{\ddagger}_{298}$, kcal/mol ^b
1a	ClCHF ₂	89	-12.0	10.1 ± 0.5 ^c
1b	CHCl ₃ -CDCl ₃	64	-13.5	12.4 ± 0.4
1e	C ₂ Cl ₄	66	-12.9	17.8 ± 0.4
1h	DMSO- <i>d</i> ₆	17	-12.8	18.0 ± 0.9
1f	C ₂ Cl ₄	63	-13.4	18.8 ± 0.9
1c	C ₂ Cl ₄	16	-13.3	19.3 ± 0.9
1d	C ₂ Cl ₄	20	-13.7	20.2 ± 1.9
1g	C ₂ Cl ₄	22	-13.9	20.8 ± 0.8

^a Sign assumed. ^b Other parameters from previous work: **1b**, $\Delta G^{\ddagger}_e = 12.1 \pm 0.2$ kcal/mol; ^{6b} **1e**, $\Delta G^{\ddagger}_e = 18.8 \pm 0.2$ kcal/mol; ^{6b} **1i**, $\Delta G^{\ddagger}_e = 10.0 \pm 0.3$ kcal/mol; ^{6c} **1j**, $\Delta G^{\ddagger}_e = 12.3 \pm 0.2$ kcal/mol. ^{6c} Subject to additional indeterminate error because line-shape analysis was limited to a temperature range above coalescence.

comparison of experimental and calculated¹⁷ decoupled allylic absorption afforded the conformational lifetimes shown in Figure 3. An Arrhenius plot (Figure 4) of the rate constants thus obtained gave on least-squares treatment the activation parameters which appear in Table III along with those of the other derivatives obtained by analogous procedures.

Observation of diketone **1a** at the slow exchange limit presented some experimental difficulty. The undecoupled spectrum in ClCHF₂ showed no major changes down to $\sim -55^\circ$, but below this temperature the allylic pattern broadened at -80° , separated into two multiplets at $\sim -120^\circ$, and finally exhibited the pattern shown in Figure 5 at -150° . The latter resembles the spectrum of **1e** at ambient temperature. Unfortunately, because of instrument limitations, line-shape analysis of decoupled allylic absorption was restricted to a temperature range, above coalescence, -70 to -95° , and the probable error of the calculated free energy of activation is consequently greater than indicated. For the calculations, the geminal coupling constant obtained from analysis of the ambient temperature spectrum was used, and $\Delta\nu_{AB}$ was estimated from separation of allylic multiplets in Figure 5 as 89 Hz. Tetraene **1b** was amenable to complete analysis, but allylic absorption was somewhat perturbed by small coupling to exocyclic olefinic protons.

Since an ABXX'B'A' spectrum is consistent with either a chair or boat conformer, the absorption of protons exterior to the ten-membered ring in the tetrahedral derivatives was examined as a possible conformational probe. Most of the evidence was suggestive but equivocal. Thus single substituent absorption patterns in the spectra of **1c**, **1d**, and **1g** (Table II) suggested the chair, but the possibility of accidental chemical shift equivalence could not be ruled out. Indeed, the appearance of -OCH₂CH₂- and -SCH₂CH₂S- singlets in the spectra of **1e** and **1f** demonstrates the latter effect. Tetraol **1h**, however, provided definitive information on this point. In the ambient temperature spectrum in DMSO-*d*₆, the hydroxymethyl absorption appeared as an ABX pattern which collapsed to an AB quartet ($\Delta\nu_{AB} = 20$ Hz, $|J_{AB}| = 10.5$ Hz) upon double irradiation of the hydroxyl proton. The indicated nonequivalence of exocyclic geminal protons is consistent with the chair but not the boat.

(17) H. S. Gutowsky, R. L. Vold, and E. J. Wells, *J. Chem. Phys.*, **43**, 4107 (1965).

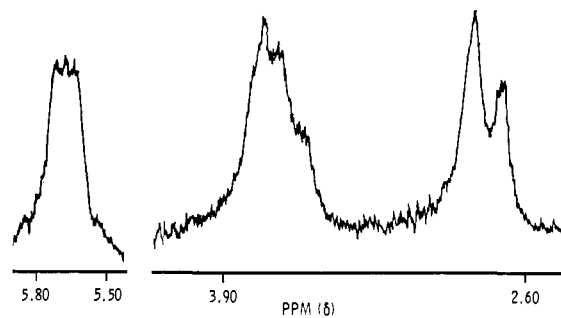


Figure 5. The 100-MHz pmr spectrum of diketone **1a** at -150° in ClCHF₂.

During determination of activation parameters for ring inversion an attempt was made to utilize the hydroxymethyl groups in **1h** as a second probe of the process. However, line-shape analysis of spin-decoupled exocyclic geminal proton absorption led to poor correlation between calculated and experimental spectra and apparent activation barriers which were somewhat higher than those gained from analysis of allylic protons. The discrepancy probably arises from onset, over the temperature range studied, of rotational and possibly hydrogen-bonding isomerism of CH₂OH groups at rates within the nmr range of detection. Such processes would modulate spectral changes due to ring inversion alone by changing $\Delta\nu_{AB}$ and possibly J_{AB} .

Discussion

The available direct experimental evidence establishing conformational preferences in *cis,cis*-1,6-cyclodecadienes is somewhat fragmentary but has consistently shown the chair to be favored. This includes examinations of diketone **1a**^{7a} and the mercuric chloride complex of dithioether **1c**^{7b} in the solid, the hydrocarbon in the gas,⁸ the hydrocarbon in solution,^{6b} and our current finding regarding tetraol **1h** in solution. Evidence concerning other derivatives is not unequivocal, but for several reasons we feel that a preference for the chair is a general feature of the ring system, at least among derivatives studied thus far. First, analysis of specific torsional and nonbonded substituent interactions suggests that the aforementioned experimentally established preference for the chair should be maintained in derivatives with like substituents at positions 4 and 9. These interactions are identical in the perfect chair and boat, but even in the predicted equilibrium boat geometry in which relief of double bond compression has reached some compromise with other developing sources of strain, models indicate that the resultant changes in substituent interactions would at least not alter relative energies of the chair and boat. Secondly, our results, and those of others,^{6b,c} reveal clear preferences for single conformers among a variety of derivatives. At the slow exchange limit, the ABXX'B'A' splitting patterns exhibited by **1b-h** were well defined, and there was no indication within instrumental limits of detection of the presence of other conformers. The low-temperature spectrum of the diketone, although not well resolved, was similar to those of the tetrahedral derivatives at ambient temperature. Finally, substituent absorption patterns were uniformly consonant with the chair (Table II), and although the evidence was unequivocal only with tetraol **1h**, we prefer the

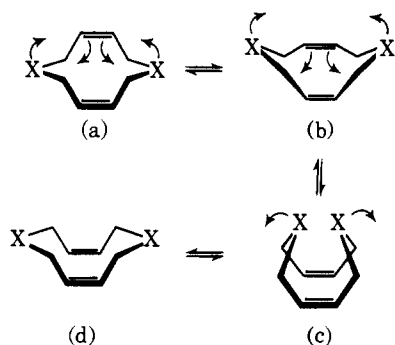
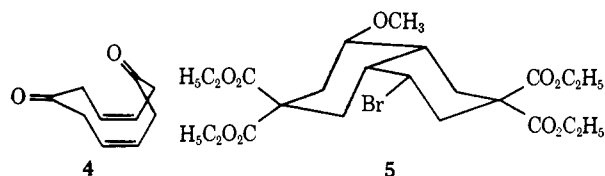


Figure 6. Itinerary for chair-boat interconversion of *cis,cis*-1,6-cyclodecadienes via synchronous double bond flipping. In the interconversion of (b) and (c), the two X groups and a *cis*-2-butene fragment become coplanar.

interpretation that the pmr spectral equivalence of substituents in **1c**, **d**, and **g** is not fortuitous but reflects a consistent conformational preference.

With regard to the foregoing considerations, the force-field calculations of Allinger, *et al.*, are instructive.^{9a} At room temperature the hydrocarbon was predicted to be a 65:35 mixture of chair and boat,¹⁸ and the diketone a 59:32:9 mixture of chair, boat, and half-boat **4**, in which one prow of the boat is tipped back over the ring. The importance of **4** relative to the hydrocarbon results from the lack of hydrogen on the carbon which is tipped back and from a favorable dipole-dipole interaction of carbonyl groups. In



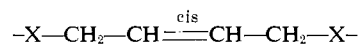
each case predominance of the chair was predicted to increase at lower temperatures. These predictions are in accord with results of previous studies of the hydrocarbon^{6b,8} and diketone^{7a} and also with our findings. As mentioned above, the low-temperature spectrum of the diketone is consistent with the chair, and the ambient temperature spectrum, while not a direct probe of conformational makeup, is compatible with a rapidly interconverting mixture of **2a**, **3a**, and **4**. While calculations were not extended to other derivatives, the consistency of theory and experiment in favoring the chair is striking and reinforces earlier qualitative arguments.^{4,5}

The rigidity and compactness of chair *cis,cis*-1,6-cyclodecadienes, as revealed by molecular models, greatly limit possible inversion mechanisms. In fact, a simple chair-boat-chair itinerary, to which we and others have alluded in earlier studies,⁶ seems to be the only pathway which avoids unrealistic structural contortions.

The flipping process connecting chair and boat embraces in principle a spectrum of mechanisms generally characterized by the timing of pseudorotation of allylic carbons and ranging at one extreme from synchronous flipping, possibly with maintenance of a molecular plane of symmetry, through processes in which pseudorotation

(18) Ermer and Lifson^{9b} have calculated the enthalpy of the chair to be only 0.16 kcal/mol lower than that of the boat, but have also noted that the functions used for nonbonded interactions may have underestimated olefin-olefin repulsion in the boat.

of one allylic carbon more or less lags behind that of the other. Experimentally, the activation parameters obtained in this study provide a valuable probe of the transition state for this inversion. As shown in Table III substituent groups X have a striking influence on free energies of activation, the values ranging over approximately 10 kcal/mol. Dale, *et al.*,^{6b} have noted the same type of effect in a series of derivatives overlapping those examined here and have pointed out a correlation between activation free energies of inversion for four carbocyclic derivatives (X = CCl₂, CH₂, C=CH₂, and C=O) and rotational barriers in -CH₂X- obtained from model compounds (3.7, 2.9, 2.2, and 0.8 kcal/mol, respectively). Since the aforementioned double bond flipping process will reasonably engender transition state substituent eclipsing interactions, such a correlation is not unusual if development of torsional strain is the only significant variable determining activation barriers. A notable exception, however, was diether **1i** which is more flexible (*T_c* ~ -70°) than predicted by the -CH₂O- rotational barrier (2.7 kcal/mol). Consideration of ways in which this discrepancy can be accommodated within a more highly defined inversion mechanism suggests to us that the magnitude of transannular nonbonded interactions involving approach of X groups toward each other contribute significantly to the observed differences in flexibility. This effect can be visualized most clearly and should be most important for the synchronous flipping (Figure 6). In this case, the segment



approaches planarity and the effect of pseudorotation of X groups toward each other is to decrease bond angle distortion at allylic and olefinic carbons within that segment to an extent limited by the steric demands of X and thus lower the inversion barrier. For nonsynchronous flipping, the effect is less predictable because of the large number of possible transition-state geometries. In many of these direct approach of X groups is not mandatory and the substituent effect would be expected to attenuate.

Certain trends among the activation parameters in Table III are consistent with the foregoing considerations. The first is the contrast in flexibility between tetrahedral derivatives (**1c-h**) on one hand and trigonal and heterocyclic derivatives (**1a, b, i, j**) on the other, a pattern which is consonant with the expected earlier development of steric interactions of tetrahedral groups in cases where the steric effect is important. Secondly, the trend of activation energies within the tetrahedral group seems generally to correlate with substituent "size." For example, the hydrocarbon (*T_c* ~ 20°)^{6b} is the most flexible of the series, and ketal derivatives **1c, d**, and **e** rank in the order expected if OC₂H₅ is larger than OCH₃ and if the steric demands of the cyclic ketal group are smaller than either as a consequence of the alkyl group being tied back in a ring. However, detailed comparisons beyond a series of structurally related derivatives such as the ketals are tenuous because the X...X interaction in question is quite different from those traditionally used to gauge conformational preferences, *i.e.*, axial-equatorial free energy differences in chair cyclohexanes. In particular, because of the mutuality and directionality of the interaction, dipolar

interactions and bond length variation (C–O, C–S, C–C) should contribute to varying extents to determining limits of X···X approach. Presumably similarity of activation energies for **1e** and its sulfur analog **1f** and the rigidity of tetraester **1g** reflect an interplay of these effects. The reasons for tetraol **1h**'s position in this scheme is, of course, highly speculative in view of solvent–substituent hydrogen bonding and the uncertainty of transition-state hydrogen-bonding effects.

The dynamics of ring inversion among tetrahedral derivatives, *i.e.*, high activation energies coupled with a significant substituent effect, are consistent with synchronous flipping as depicted in Figure 6. Another noteworthy finding from these results is the high flexibility of diketone **1a**. The latter is revealed not so much by comparison of free energies of activation in Table III, where the value for **1a** is subject to additional indeterminate error, as by the contrast in estimated coalescence temperatures for spin-decoupled allylic absorption (**1a**, $< -100^\circ$; **1b**, $\sim 17^\circ$). Synchronous flipping in **1a** does not seem consistent with a barrier significantly lower than that of tetraene **1b** in view of the dipole–dipole repulsion which would arise on direct approach of carbonyl groups. Consequently, the lower barrier for **1a** seems better accommodated by the aforementioned sequential flipping mechanism with minimization of C=O dipole repulsion. While the nature of C=O interactions involved in this pathway is necessarily ill-defined, the fact that tetraene **1b** does not exhibit a similar flexibility suggests two possibilities. The first is that the transition state C=O dipole–dipole interaction for **1a** is in fact attractive, and the second is that the greater nonbonded interactions of C=CH₂ *vs.* C=O constrain the tetraene to a more symmetrical flipping process.

Another structural variable which has been suggested to influence the transition state for inversion of *cis,cis*-1,6-cyclodecadienes is bond angles at positions 4 and 9. Lehn and Feigenbaum, in a study of heterocycles **1i** and **1j**,^{6c} have suggested that these angles widen in the transition state on the basis that the barrier in the diether ($\angle \text{COC} \simeq 112^\circ$) is smaller than that in the dithioether ($\angle \text{CSC} \simeq 105^\circ$) (see footnote in Table III) although the –CH₂O– rotational barrier is higher than that of –CH₂S–. The importance of this effect, however, is not clear, since a larger transannular sulfur–sulfur interaction could produce the same trend. In this connection it is interesting that calculated chair–boat energy differences for the diketone and hydrocarbon are virtually identical (~ 0.35 kcal/mol),^{9a} although one might naively expect a narrowing of this difference in the diketone because of a decrease in transannular nonbonded interactions brought about by widening of angles at C-4 and C-9. Clearly, any well-differentiated effect of this variable is not yet apparent.

Finally, it may be noted that the influence of conformational properties on chemical behavior in *cis,cis*-1,6-cyclodecadienes is significant, as shown by studies on the photochemistry of diketone **1a**¹⁹ and on electrophilic addition to tetraester **1g**.^{10b} The latter investigation is particularly interesting in revealing the unusually congested environments of double bonds in the chair and boat. **1g** failed to take up bromine in carbon tetra-

chloride but reacted with bromine in methanol to give *cis*-decalin **5**. Evidently, steric shielding by axial hydrogens prevents completion of *trans* 1,2-addition to the chair, the only feasible addition pathway taking place across mutually shielded double bonds in the boat in a 1,4-manner with participation of solvent.

Experimental Section

All pmr spectra were recorded on a Varian Associates HA-100 spectrometer equipped with a Model V4343 variable-temperature accessory. Temperatures were determined by measuring peak separations in methanol (low-temperature region) or ethylene glycol (high-temperature region). Spectra were recorded in the frequency sweep mode with an internal lock. Chemical shifts obtained from ambient temperature spectra are given in Table II.

Calculations of spectra were carried out on a Honeywell 800 computer. The program of Swalen and Reilly²⁰ was used to calculate line spectra, and the program of Gutowsky, *et al.*,¹⁷ was used for line-shape analysis. Activation parameters were computed with the weighted least-squares program by De Tar.²¹

All infrared spectra were recorded on a Perkin–Elmer Model 337 spectrometer.

Elemental analyses were performed by Elek Microanalytical Laboratories, Torrance, Calif.

cis,cis-Cyclodeca-1,6-diene-4,9-dione (**1a**). An improved procedure for preparing this compound directly from *trans*- $\Delta^{2,6}$ -hexalin-9,10-diol⁵ is described here.

To 10.5 g (63 mmol) of the *trans* diol and 31 g of trichloroacetic acid dissolved in 250 ml of dry 1,2-dimethoxyethane was added slowly with cooling and magnetic stirring 42 g (95 mmol) of lead tetraacetate. The resulting solution was sealed and stirred at ambient temperature for 4 hr, at which point excess lead tetraacetate (as indicated by a positive starch–potassium iodide test) was destroyed by addition of ethylene glycol. The mixture was then cooled to -78° and the resulting white precipitate was collected by suction filtration, suspended and washed in 50 ml of water, and re-collected to give 8.5 g (82%) of crude diketone. Recrystallization from acetone followed by sublimation ($60\text{--}80^\circ$ (2 mm)) gave the pure material (58%), mp $182\text{--}185^\circ$ (lit.⁵ mp $183\text{--}185^\circ$).

cis,cis-4,9-Dimethylenecyclodeca-1,6-diene (**1b**). To 9.90 g (28 mmol) of triphenylphosphonium bromide in 600 ml of anhydrous ether (distilled from LiAlH₄) was added 13 ml of a solution of phenyllithium in benzene–ether (2.14 M, Alfa Inorganics, Inc.) under gentle nitrogen flow. To the resulting yellow solution was added 1.5 g (9.3 mmol) of diketone **1a** suspended in 150 ml of anhydrous ether. The reaction mixture was then stirred at ambient temperature for 24 hr under a nitrogen atmosphere, during which time the solution turned light brown. After filtration to remove gelatinous material, the solution was stirred over lithium chloride for 6 hr and filtered again. The filtrate was partially concentrated under aspirator pressure on a rotary evaporator, and residual ether was then removed at aspirator pressure in a sublimation apparatus equipped with a collection surface at -78° . The apparatus was then evacuated to 0.5 mm whereupon clear square-shaped crystals deposited on the collecting finger. Resublimation afforded 0.61 g (42%) of finely divided white crystals, mp $65\text{--}67^\circ$. Another sublimation yielded the analytical sample, mp $67.5\text{--}69.0^\circ$; $\nu_{\text{max}}^{\text{COC}}$ 3070, 3000, 1645, and 896 cm^{-1} .

Anal. Calcd for C₁₂H₁₆: C, 89.94; H, 10.06. Found: C, 89.72; H, 10.28.

cis,cis-4,4,9,9-Tetramethoxycyclodeca-1,6-diene (**1c**). This compound was prepared by cleavage of *trans*- $\Delta^{2,6}$ -hexalin-9,10-diol with lead tetraacetate in the presence of methanol and trichloroacetic acid according to the procedure of Grob and Schiess,⁵ mp $200.5\text{--}201.0^\circ$ (lit.⁵ mp $197\text{--}200^\circ$).

cis,cis-4,4,9,9-Tetraethoxycyclodeca-1,6-diene (**1d**). Diketone **1a** (1.00 g, 6.1 mmol) was added to 300 ml of absolute ethanol containing a small crystal of *p*-toluenesulfonic acid monohydrate, and the resulting solution was sealed and stirred magnetically for 5 days at ambient temperature. The reaction mixture was then cooled in a freezer, and the colorless crystals which formed were collected by suction filtration to give 513 mg (27%) of crude diketal. The filtrate contained a mixture of diketal and diketone as indicated by ir analysis. Recrystallization from absolute ethanol

(19) J. R. Scheffer and M. L. Lungle, *Tetrahedron Lett.*, 845 (1969).

(20) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

(21) D. F. De Tar, *J. Chem. Educ.*, **44**, 759 (1967).

afforded the pure material: mp 103–105°; $\nu_{\text{max}}^{\text{KBr}}$ 3020, 1168, 1140, 1098, 1066, 1057, and 1042 cm^{-1} .

Anal. Calcd for $\text{C}_{18}\text{H}_{22}\text{O}_4$: C, 69.19; H, 10.32. Found: C, 69.09; H, 10.56.

cis,cis-4,4,9,9-Bis(ethylenedioxy)cyclodeca-1,6-diene (1e). Diketone **1a** (162 mg, 1 mmol) was partially dissolved in 20 ml of ethylene glycol and 0.5 ml of boron trifluoride etherate was added. The resulting solution was sealed, stirred at ambient temperature for 2.5 hr, and cooled to 0°, and the resulting precipitate was collected by suction filtration to give 227 mg (91%) of diketal, mp 187°. Recrystallization from carbon tetrachloride afforded the analytical sample as fluffy, colorless crystals: mp 185.5–186.0° subl; $\nu_{\text{max}}^{\text{CHCl}_3}$ 1200–1230 (b), 1140, 1060, and 1030 cm^{-1} .

Anal. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4$: C, 66.65; H, 7.99. Found: C, 66.76; H, 7.99.

cis,cis-4,4,9,9-Bis(thioethylenedioxy)cyclodeca-1,6-diene (1f). Diketone **1a** (1.0 g, 6.1 mmol) was dissolved in 100 ml of chloroform containing 20 ml of 1,2-ethanedithiol and 1.0 ml of boron trifluoride etherate. The reaction mixture was then sealed and allowed to stand at ambient temperature for 2 hr. Solvent was then removed with the aid of a rotary evaporator and the resulting precipitate was collected by suction filtration to give 1.92 g (99.5%) of colorless crystals, mp 239–240°. Recrystallization from chloroform afforded 1.62 g (84%) of pure dithioketal, mp 240.5–242.0° subl (lit.^{10c} mp 244–245°).

cis,cis-4,4,9,9-Tetracarboethoxycyclodeca-1,6-diene (1g). The

tetraester was prepared in 2.1% yield by condensation of diethyl malonate with *cis*-1,4-dichloro-2-butene according to the procedure of Gipson;^{10c,22} colorless plates, mp 158–160° (lit.^{10c} mp 161–162°).

cis,cis-4,4,9,9-Tetrakis(hydroxymethyl)cyclodeca-1,6-diene (1h). The tetraol was prepared by the method of Gipson.^{10c} A solution of 216 mg (5.7 mmol) of lithium aluminum hydride in 50 ml of dry tetrahydrofuran was prepared in a 100-ml, three-necked, round-bottomed flask equipped with a condenser, a magnetic stirrer, and an addition funnel. The system was placed under a nitrogen atmosphere, and a solution of 385 mg (0.91 mmol) of tetraester **1g** in 20 ml of dry tetrahydrofuran was added through the dropping funnel. The resulting mixture was then refluxed with stirring for 24 hr. After cooling to room temperature and cautious addition of 3 ml of absolute ethanol, the mixture was stirred for 15 min. Then 20 ml of 2 *N* hydrochloric acid was added and the mixture refluxed for 1 hr. After the mixture was cooled to room temperature and concentrated to about one-half the original volume on a rotary evaporator, 230 mg of a white precipitate was collected by suction filtration. Recrystallization from methanol and drying over phosphorus pentoxide under vacuum afforded 110 mg (48%) of the tetraol as colorless crystals, mp 254–257° (lit.^{10c} mp 261–262°).

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(22) A similar procedure for making this compound may be found in ref 10a.

Phosphorus Large Membered Ring Molecules. 12- and 18-Membered Ring Phosphonites and the Corresponding Phosphonothioates

J. P. Albrand, J. P. Dutasta, and J. B. Robert*

Contribution from the Département de Recherche Fondamentale, Laboratoire de Chimie Organique Physique, Centre d'Etudes Nucléaires, F.38041 Grenoble Cedex, France. Received January 30, 1974

Abstract: 2,5,5-Trimethyl-1,3,2-dioxaphosphorinane exists in equilibrium with its dimeric and trimeric forms which are 12- and 18-membered rings, respectively. The corresponding 2-thiono derivatives have been prepared and isolated. These large membered rings exist in different diastereomeric forms which display distinct ³¹P nmr signals. The two diastereoisomers of the 12-membered ring thiono derivatives have been separated.

The tendency of cyclic phosphonites to polymerize has been noted by different authors.¹ In particular, in a study of six-membered cyclic phosphonites,² White reported some experimental features concerning the polymerization process of 2,5,5-trimethyl-1,3,2-dioxaphosphorinane (**1**) and showed that this process is a reversible one. He also suggested that the polymeric species observed are phosphonites, but did not further elucidate their structure (long chain or macrocyclic).

As part of our studies on six-membered cyclic phosphorus compounds,³ we report here data which show the existence of dimeric (12-membered ring) and trimeric (18-membered ring) phosphonite molecules

among the polymeric species obtained in the polymerization process of **1**. The corresponding phosphonothioates have been isolated and characterized.

Results

Our observations on the evolution of pure samples of **1**, on standing, are very close to those reported by White. For samples of very good purity, sealed off under vacuum, the polymerization may be a very slow process since some of our samples remained quite mobile liquids after several months at room temperature. As reported previously,² the redistillation *in vacuo* of polymerized samples allows a nearly quantitative recovery of pure mobile **1**.

A freshly prepared benzene solution of **1** (sample I) shows only the nmr features expected for **1** (Figure 1a). In particular, the ¹H noise-decoupled ³¹P spectrum is a sharp singlet (δ –163 ppm). When such a benzene solution of **1** is left for a few days in a tube sealed under vacuum, additional nmr lines appear in the proton and phosphorus spectra in addition to the lines of species **1**.

(1) T. Mukaiyama, T. Fujisawa, Y. Tamura, and Y. Yokota, *J. Org. Chem.*, **29**, 2572 (1964); A. N. Pudovik and G. I. Evstaf'ev, *Vysokomol. Soedin.*, **6** (12), 2139 (1964); A. Zwierzak, *Can. J. Chem.*, **45**, 2501 (1967); H. J. Harwood and N. K. Patel, *Macromolecules*, **1**, 233 (1968); J. E. Newbery, R. Woodcock, and R. F. Hudson, *Chem. Commun.*, 22 (1969); W. G. Bentrude, K. G. Yee, R. D. Bertrand, and D. M. Grant, *J. Amer. Chem. Soc.*, **93**, 797 (1971).

(2) D. W. White, *Phosphorus*, **1**, 33 (1971).

(3) R. O. Hutchins, B. E. Maryanoff, J. P. Albrand, A. Cogne, D. Gagnaire, and J. B. Robert, *J. Amer. Chem. Soc.*, **94**, 9151 (1972).