

on the above system in the conventional manner using photon counting. For the circular dichroism measurements the plane polarized laser beam was passed through a potassium dideuterium phosphate electro-optical modulator before being focused on the sample. The electro-optical modulator was driven by the amplified 500-Hz internal oscillator signal of a lock-in amplifier. The amplitude of the ac voltage applied to the electro-optical modulator was set at the "quarter-wave potential" corresponding to the laser wavelength, 4880 Å. The light illuminating the sample therefore alternated between right and left circularly polarized 500 times a second. This arrangement generates three main signals at the output of the photomultiplier tube: (a) a dc component proportional to the sum of the Raman intensities due to right and left circularly polarized incident light (the normal Raman effect); (b) a 1000-Hz component, the amplitude of which depends on both the intensity and the depolarization ratio of the Raman line; and (c) a 500-Hz component proportional to the difference in the Raman intensities with right and left circularly polarized light incident on the sample, as well as higher harmonics. The lock-in amplifier rejects all components of the composite output signal except that at 500 Hz which is in phase with the signal impressed upon the electro-optical modulator and, hence, will display directly the difference in Raman intensity for right and left circularly polarized light incident on the sample. The phase sensitivity of the amplifier will, moreover, indicate the sign of the difference between the scattered intensities due to right and left circularly polarized light, that is, the sign of the Raman circular dichroism.

The Raman circular dichroism may be expressed in two ways, either as the observed quantity $I_r - I_l$, where I_r and I_l are the intensities of the scattered light with right and left circularly polarized incident light respectively, or preferably as a normalized dimensionless quantity Δ ,^{2,4} where

$$\Delta = (I_r - I_l)/(I_r + I_l)$$

This latter quantity which is similar to the "dissymmetry factor," g , in electronic circular dichroism, can be defined for both parallel, $\Delta_{||}$, and perpendicular, Δ_{\perp} , polarization.

In Figure 1 we show the normal Raman spectrum in both polarizations and the Raman circular dichroism spectra for α -phenylethylamine in the (\pm) , $(+)$, and $(-)$ forms of the pure liquids in parallel polarization. In addition, we give an approximate normalized spectrum, $\Delta_{||}$, measured by dividing the peak heights of the circular dichroism spectrum by the normal Raman spectrum in parallel polarization. [Δ can be measured directly by (electronically) combining the dc and ac signals.] In perpendicular polarization the Raman circular dichroism is at least 100 times weaker and was barely detectable even in the strongest line. As may have been expected and was theoretically predicted,^{2,4} the Rayleigh line, anti-Stokes lines, and the Stokes lines all show Raman circular dichroism, and the corresponding lines in the anti-Stokes and Stokes regions have the same sign. Two arresting features are also observed; every line in all regions of the spectrum has the same sign for a given enantiomer and those lines

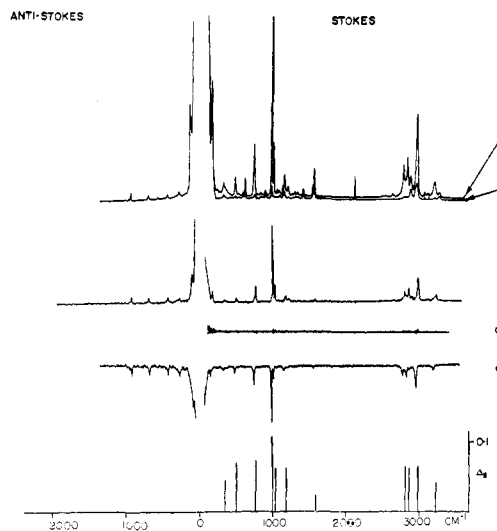


Figure 1. The spectra are as follows: (a) the normal Raman spectrum in parallel polarization of α -phenylethylamine, (b) the normal Raman spectrum of the same molecule in perpendicular polarization, (c) the Raman circular dichroism spectrum of $(-)$ - α -phenylethylamine in parallel polarization, (d) the Raman circular dichroism of (\pm) - α -phenylethylamine in parallel polarization, (e) the Raman circular dichroism of $(+)$ - α -phenylethylamine in parallel polarization, and (f) the normalized Raman circular dichroism, Δ , in parallel polarization for $(-)$ - α -phenylethylamine. Note: lines undermarked by dots in (a) are due to fluorescent room illumination.

which are more strongly polarized are also those which show the stronger Raman circular dichroism. We have found this to be true for five other compounds where we have observed the effect, α -phenylethylamine showing the strongest effect. All these molecules, however, were devoid of any symmetry elements and formally all the transitions belonged to the totally symmetric representation. It may turn out that dissymmetric molecules of higher symmetry will show Raman circular dichroism of opposing sign within the same spectrum. Whatever the case, the possible use of this technique in the assignment of vibrational spectra and its application to the designation of the absolute configurations and structures of large and small molecules presents an exciting prospect.

Acknowledgments. We thank Beckman instruments for the loan of a Raman spectrometer and the Chemistry Department who supported most of this work and also the N.R.C. We are grateful to Mr. W. Panning and Mr. S. Gyarmati for help in the design and construction of the electronics.

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The Energy Barrier to Racemization in a *vic*-Dialkylidenecycloalkane Analog. 3,4-Diisopropylidene-8-phenyl-1,6,8-triazabicyclo-[4.3.0]nonane-7,9-dione

Sir:

A type of molecular dissymmetry which appears so far to have escaped quantitative study is that shown by appropriately substituted *vic*-dialkylidenecycloalkanes

(4) L. D. Barron, *J. Chem. Soc. A*, 2889 (1971).

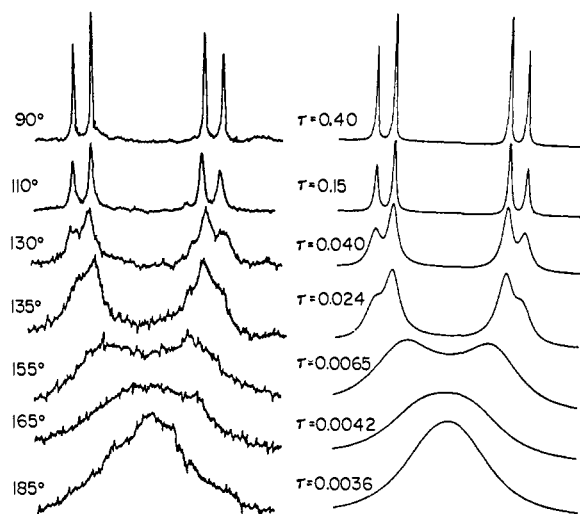
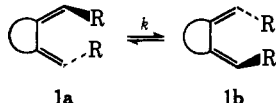
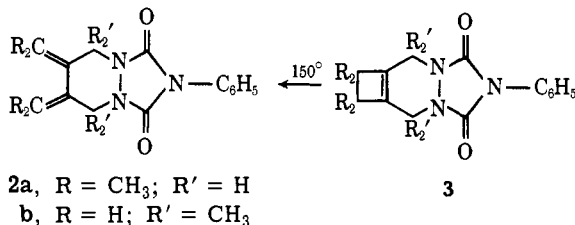


Figure 1. Experimental (left) and calculated nmr spectra of the methylene protons of **2a**. Constant parameters assumed for the latter were: sweep width = 500 Hz, $J_{AB} = 12.3$ Hz, $\Delta\nu_{AB} = 92$ Hz, $T_2 = 0.45$ sec.

(1). Though it was recognized at least 20 years ago that such systems should be capable of enantiomerism,¹



intensive efforts to prepare a representative optically active example were unsuccessful.² Other reports on similarly constituted dienes have commented on the effects of nonplanarity on their Diels–Alder reactivity,³ uv^{4,5} and nmr spectra,⁵ but not on their concomitant chirality. We now report nmr measurement of the rate of racemization of a heterocyclic analog of **1** (**2a**, below),



prepared by thermal isomerization of the Diels–Alder adduct **3a** of 1,2-dimethylene-3,3,4,4-tetramethylcyclobutane⁶ and 4-phenyl-1,2,4-triazoline-3,5-dione.^{7,8}

The nmr spectrum of **2a** at ambient temperature in CCl₄ shows, in addition to phenyl absorption, methyl resonances at τ 8.20 and 8.40 and nonequivalent methylene proton signals at τ 5.40 and 6.24 ($|J_{gem}| = 12.3$ Hz). Models suggest that the preferred conformation

- (1) K. B. Alberman, R. N. Haszeldine, and F. B. Kipping, *J. Chem. Soc.*, 3287 (1952).
- (2) F. B. Kipping and J. J. Wren, *ibid.*, 3246 (1957).
- (3) I. N. Nazarov and N. V. Kuznetsov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 236 (1960).
- (4) W. F. Forbes, R. Chilton, and A. Balasubramanian, *J. Org. Chem.*, **29**, 3257 (1964).
- (5) J. E. Starr and R. H. Eastman, *ibid.*, **31**, 1393 (1966).
- (6) (a) E. F. Kiefer and C. H. Tanna, *J. Amer. Chem. Soc.*, **91**, 4478 (1969); (b) E. F. Kiefer and J. Y. Fukunaga, *Tetrahedron Lett.*, 993 (1969).
- (7) R. C. Cookson, S. S. H. Gilani, and I. D. R. Stevens, *J. Chem. Soc. C*, 1905 (1967).
- (8) Synthetic details will be reported later. All intermediates were routinely characterized by their nmr, ir, uv, and mass spectra.

of the six-membered ring in **2a** is a half-chair in which the dihedral angle between the π bond planes is *ca.* 50°; the two equatorial protons lie nearly in the nodal plane of the adjacent π bond and the axial protons nearly perpendicular to the plane. Consequently, only the high-field (axial) protons show homoallylic coupling to the methyl groups⁹ ($|J| = 1.7$ and 0.4 Hz). To eliminate complications arising from possible temperature dependence of homoallylic coupling, the methylene signals were reduced to a simple AB quartet for kinetic line-shape analysis¹⁰ by double resonance at the average methyl frequency.¹¹ The least-squares Arrhenius plot for 11 points over the range 120–170° gave $E_a = 21.1 \pm 0.9$ kcal/mol, $\log A = 12.9 \pm 0.4$ (see Figure 1; instabilities in the sample and temperature regulation hampered a closer approach to the fast-exchange limit).

It is well known that substantial energy barriers are associated with N–N bond rotation in monocyclic piperidazines and other substituted hydrazines.¹² Such a process is effectively prevented by the fused five-membered ring in **2**, and an alternative conformational change resulting from simultaneous inversion of both nitrogen atoms can be ruled out by the nmr spectra. Nonetheless, an experimental estimate for the ring inversion barrier for **2a** in the absence of exocyclic methyl–methyl interaction was desirable; it was obtained from the temperature-dependent nmr spectrum of **2b**. The coalescence temperature could not be reached in any solvent polar enough to produce useful concentrations of **2b**; however, at -140° in dichlorofluoromethane, the methyl singlet of **2b** was broadened to 26 Hz, which, if taken as the minimum methyl line separation for the individual enantiomers, leads to a maximum energy barrier of 6.5 kcal/mol, assuming $\log A(\mathbf{2b}) = \log A(\mathbf{2a})$. Given the uncertainties in the true line separation, coalescence temperature, and T_2 (minor broadening of other spectral lines was also observed at -140°), the actual energy barrier in **2b** is probably closer to 5.5 kcal/mol, about the same as that of cyclohexene.¹³ Thus, the large energy barrier in **2a** is due almost entirely to the close approach of the “inside” methyl groups in the transition state. The value for **2a** appears to be consistent with that obtained for racemization of the analogously constituted 9,10-dihydro-4,5-dimethylphenanthrene (23.1 kcal/mol);¹⁴ however, this agreement is possibly fortuitous, since both ground and transition states are more strained in the latter system due to its greater overall structural rigidity.¹⁵

It is worth noting that four-membered ring examples of **1**, *e.g.*, 1,2-diisopropylidencyclobutane and its 3,3,-

(9) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(10) The program was written for the IBM 360 following the treatment of R. M. Lynden-Bell, *Progr. Nucl. Magn. Resonance Spectrosc.*, **2**, 163 (1967).

(11) The solvent and frequency-sweep lock signal for the high-temperature experiments was biphenyl, in which the separation of the methyl signals at 70° is only 8 Hz at 100 MHz. We thank Mr. James Loo for performing the nmr experiments. The Varian HA-100 spectrometer used was purchased with funds made available under National Institutes of Health Grant No. GM-14533. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(12) (a) J. E. Anderson and J. M. Lehn, *Tetrahedron*, **24**, 123, 137 (1968); (b) E. W. Bittner and J. T. Gerig, *J. Amer. Chem. Soc.*, **94**, 913 (1972).

(13) (a) F. A. L. Anet and M. Z. Haq, *ibid.*, **87**, 3147 (1965); (b) F. R. Jensen and C. H. Bushweller, *ibid.*, **91**, 5774 (1969).

(14) K. Mislow and H. B. Hopps, *ibid.*, **84**, 3018 (1962).

(15) K. Mislow, R. Graeve, A. J. Gordon, and G. H. Wahl, Jr., *ibid.*, **86**, 1733 (1964).

4,4-tetramethyl derivative,⁶ racemize rapidly at room temperature on the nmr time scale, indicating energy barriers of <12 kcal/mol. This behavior is consistent with the observation that the closest approach of vinyl methyl groups in these compounds is 2.5 Å without exocyclic bond deformation; the corresponding distance in a coplanar transition state for **2a** is only 1.4 Å. Extension of this work and optical resolution of other systems of type **1** are planned.

(16) American Chemical Society–Petroleum Research Fund Fellow, 1969–1970.

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Dimerization of 1,2-Cyclohexadiene, a Model for Nonconcerted Allene Dimerization. Determination of a Secondary Deuterium Kinetic Isotope Effect by Deuterium Nuclear Magnetic Resonance¹

Sir:

The dimerization of allenes to 1,2-dimethylenecyclobutanes has evoked much mechanistic interest.² In particular, one question arises repeatedly: does the addition occur in one step or is it a multistep process involving at least one intermediate? Dolbier and Dai³ in seeking to answer this question found a negligible intermolecular secondary deuterium isotope effect in the partial dimerization of mixtures of allene-*d*₄ and -*d*₀. However, dimerization of allene-1,1-*d*₂ established that an intramolecular isotope effect was operative. In terms of forming the doubly allylic C–C bond, they reported an isotope effect of $k_H/k_D = 1.14$. From these observations, they concluded that the reaction must involve a rate-determining step devoid of isotopic discrimination followed by a product-forming step which is not. However, this conclusion is not mandatory; a one-step (concerted) mechanism could lead to the observed isotope effects.⁴ Additionally, the fact that a normal intramolecular isotope effect is observed for a system undergoing an $sp^2 \rightarrow sp^3$ change is also puzzling. Both normal and inverse intermolecular isotope effects have been observed for a variety of (2 + 2) cycloadditions.⁵ For example, the addition of diphenylketene to styrene shows, as expected, an inverse isotope effect at the β position of styrene, but surprisingly a substantial normal isotope effect is found at the α position. In

(1) Acknowledgment is made to the National Science Foundation for support of this research (GP 25216).

(2) (a) For a comprehensive review, see J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1970). (b) For our preceding work, see W. R. Moore, R. D. Bach, and T. M. Ozretich, *J. Amer. Chem. Soc.*, **91**, 5918 (1969).

(3) W. R. Dolbier, Jr., and S. H. Dai, *ibid.*, **92**, 1774 (1970).

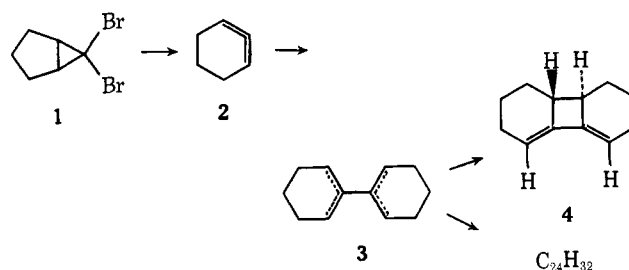
(4) One of us has pointed out (private communication to Professor Dolbier cited in footnote 13 of ref 3) that a one-step mechanism could accommodate the data provided that $(k_H/k_D)_A(k_H/k_D)_V \approx 1$, where $(k_H/k_D)_A$ is the isotope effect at the methylene group involved in forming the doubly allylic bond and $(k_H/k_D)_V$ is that at the vinylic position. This possibility was rejected³ on the grounds that a one-step mechanism would not have $(k_H/k_D)_A > 1$. However, normal isotope effects have been observed in reactions considered to be concerted; cf. ref 5d.

(5) (a) T. J. Katz and R. Dessau, *J. Amer. Chem. Soc.*, **85**, 2172 (1963); (b) W. R. Dolbier, Jr., and S. H. Dai, *ibid.*, **90**, 5028 (1968); (c) E. K. von Gustorf, D. V. White, J. Leitich, and D. Henneburg, *Tetrahedron Lett.*, 3113 (1969); (d) J. E. Baldwin and J. A. Kapecki, *J. Amer. Chem. Soc.*, **92**, 4874 (1970).

this case Baldwin has provided an interesting rationale in terms of a concerted process.^{5d}

Clearly the lack of experimental models complicates the interpretation of such isotope effects. Because of the mechanistic importance of the case of allene dimerization, we deemed it to be of prime importance to try to obtain experimental evidence establishing the nature of the intramolecular isotope effect in the product-forming step of a related reaction where independent evidence indicates that an intermediate is involved. In general, finding such model systems will not be easy. Fortunately, in this instance one can be developed.

In prior work,⁶ we have presented compelling evidence that when 1,2-cyclohexadiene (**2**) is generated from dibromide **1**, it rapidly dimerizes to an intermediate diallylene **3** which can either cyclize to diene **4** or dimerize to two C₂₄H₃₂ stereoisomers. Although **2** certainly is not a typical allene, **3** should provide an excellent model for possible intermediates formed in the dimerization of normal allenes.⁷



Labeled dibromide-1-*l-d* was treated with methyl-lithium in refluxing ether (generating 2-*l-d* as an intermediate) and the dimer 4-*d*₂ was isolated and purified.⁸ Similarly, to provide a standard for analytical purposes, dimer fully labeled at the vinyl and tertiary positions, 4-*d*₄, was prepared from 1-*l*,5-*d*₂.⁸

The proton nmr spectrum of the *d*₀ dimer (Figure 1) shows that the signals due to the tertiary allylic protons are not resolved⁹ from the complex signals of the remaining more shielded protons, making it impossible to make an accurate determination of the deuterium distribution by this indirect method. To solve this problem, we turned to deuterium nmr. Scattered examples of dmr have appeared in the literature,¹⁰ but its great potential has not been exploited nor even recognized presumably because the sensitivity to D is low,

(6) W. R. Moore and W. R. Moser, *ibid.*, **92**, 5469 (1970); *J. Org. Chem.*, **35**, 908 (1970).

(7) Although dimer **4** is not formed quantitatively from **1**, it is stable to the reaction conditions, making it a valid monitor of an intramolecular kinetic isotope effect. A meaningful intermolecular kinetic isotope effect cannot be determined since the rate-determining step probably precedes formation of **2** which also has other reaction paths open to it.

(8) (a) Dibromides 1-*l-d* and 1-*l*,5-*d*₂ were prepared by addition of dibromocarbene to the deuterated cyclopentenes. Cyclopentene-1-*d* was prepared by the xanthate dehydration of cyclopentanol-1-*d*, obtained from reduction of cyclopentanone with LiAlD₄. Cyclopentene-1,2-*d*₂ was prepared by reduction of 1,2-dibromocyclopentene with sodium in 1-methylcyclohexanol-*O-d*. (b) In each case dimer **4** was isolated by reduced pressure distillation and purified by recrystallization from methanol followed by sublimation twice. No impurities could be detected spectroscopically or by glc. (c) Low voltage mass spectral analysis: 4-*d*₂, 94.8% *d*₂, 5.2% *d*₁; 4-*d*₄, 96.5% *d*₄, 3.5% *d*₃.

(9) Partial, but inadequate, resolution was obtained in benzene.

(10) P. Diehl and Th. Liepert, *Helv. Chim. Acta*, **47**, 545 (1964); R. C. Dougherty, G. D. Norman, and J. J. Katz, *J. Amer. Chem. Soc.*, **87**, 5801 (1965); L. K. Montgomery, A. O. Clause, A. M. Crelier, and L. E. Applegate, *ibid.*, **89**, 3453 (1967); R. Wyld and J. Grinaud, *C. R. Acad. Sci., Ser. C*, **271**, 597 (1970); E. Casadevall and P. Metzger, *Tetrahedron Lett.*, 4199 (1970); R. E. Santini, *Anal. Chem.*, **43**, 801 (1971).