rides[9] and *endo-p*-bromobenzenesulfonates.[12] Rate data further indicate that there is little driving force toward solvolysis by participation of the π electrons of the benzene ring in solvolysis of the ethanodihydroanthracenes. Some participation might have been anticipated by analogy with the participation observed in *exo*-dehydronorbornyl systems, although the analogous bicyclo[2.2.2]octenyl systems have not been studied and may indeed show no such participation.[13]

Acknowledgments.—The authors are indebted to the Office of Naval Research, U. S. Navy, and to the National Science Foundation for support of this work.

Experimental

Preparation of Compounds.—The preparation of the materials used in these studies will be reported elsewhere. In general the chlorosulfides were prepared by addition of *p*-toluenesulfenyl chloride to the corresponding olefin or of thiocresol to the chloroölefin. The sulfones were prepared by oxidation of the chlorothioether with hydrogen peroxide.

Rate constants for elimination were measured as follows. A weighed amount of the β-chlorosulfone, from 0.1 to 0.8 mmole, was placed in a 100-ml. volumetric flask and 50 ml. of dioxane, measured at the temperature of the run, was added. About 40 ml. of 92.6% (by wt.) ethanol was then added, and the flask was placed in a 12.1° rate bath thermostatically controlled to a ±0.05°. After solution was complete and the contents had come to the temperature of the bath, a measured amount of ethanolic sodium hydroxide (normality calculated at 12.1°) was added followed by enough 92.6% ethanol (kept at 12.1°) to bring the volume up to the mark on the flask. The flask was removed from the bath and was shaken vigorously for several seconds. It was immediately replaced in the bath and, because the rates were fast, the first sample usually was taken almost immediately thereafter.

Since room temperature, in the case of the 12.1° runs, was about 20°, an asbestos-wrapped 10-ml. pipet was used for sampling. The samples were pipetted directly into 5 ml. of 3 *N* nitric acid contained in a 100-ml. erlenmeyer flask, the time being recorded the instant the sample started to flow from the pipet. The same pipet was used for all samples. The tip of the pipet was blown out to allow rapid drainage. The samples were analyzed for chloride ion by the Volhard procedure. Calculations of rate constants were made as described previously.[1,4]

The rate studies at 0° were run similarly except that an ice-water bath was employed in a room held at 2°.

Rate constants for solvolysis were measured as follows: A sample of the β-chlorothioether (about 0.2 mmole) was weighed into a 50-ml. volumetric flask and 50 ml. of 85% (by wt.) ethanol[14] was added at room temperature. After solution of the thioether had occurred, nine 5.5-ml. samples were removed and placed in 15 × 125 mm. Pyrex test-tubes which were then sealed. All tubes in any particular run were then placed in an oil-bath thermostatically maintained at 116.5 ± 0.05°. Tubes were removed at measured time intervals and were placed in a cold chest until the run was finished. The tubes were then opened and warmed to 20° and exactly 5 ml. was pipetted out of each into flasks for titration. Each sample was diluted with 25 ml. of ordinary ethanol, 2 drops of a mixed indicator (0.075% brom cresol green and 0.05% methyl red in ethanol) was added and the sample was titrated with aqueous 0.01 *N* sodium hydroxide. The first-order rate constants fell off with time, presumably due to reaction of ethanol with the hydrochloric acid produced in the solvolysis. The first-order plots were straight lines for the initial period of the reaction, however, and the straight-line portions were used to calculate the rate constants. It has been estimated that these results are accurate to ±30%.

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[12] S. Winstein, H. M. Walborsky and K. Schreiber, THIS JOURNAL, **72**, 5795 (1950).

[13] For a discussion of the corresponding saturated systems, see H. M. Walborsky, *Experientia*, **9**, 209 (1953).

[14] This solvent was chosen, in place of the more customary 80% ethanol, in order to effect solubility of the difficultly soluble ethanoanthracene derivatives.

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORIES, HARVARD UNIVERSITY]

The Relative Stabilities of *cis* and *trans* Isomers. III. The Cyclodecenes

BY NORMAN L. ALLINGER[1,2]

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The equilibrium constant for the reaction *trans*-cyclodecene $\rightleftarrows$ *cis*-cyclodecene has been determined to be >200 (25°). The dipole moments and other physical properties of the isomers were measured, and the relationships between these various quantities are discussed.

Introduction

It has long been a goal of organic chemists to be able to predict which of the various possible stereoisomeric structures exists in a given compound, either by a consideration of the reactions used to prepare the compound, or by an examination of its physical properties. Thus far no really general methods for accomplishing these purposes have been found. There have been evolved instead numerous rules for determining which of the various stereochemically possible products will result from a given reaction[3] and other rules which may be used to determine structure from physical properties.[4] Among the rules of the latter type, that of von Auwers was the earliest[4a] and it saw considerable service. It became clear at an early date however that exceptions to von Auwers rule existed,[5] nevertheless a great many structures were assigned using this rule some of which subsequently have been shown to be incorrect. When these incorrect assignments were uncovered several workers restated the rule in modified forms in an attempt to obtain a really useful

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[1] Department of Chemistry, Wayne State University, Detroit 2, Mich.

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[3] For a recent discussion of this subject see P. B. D. de la Mare in W. Klyne, "Progress in Stereochemistry," Butterworths Scientific Publications, London, 1954, pp. 90–125.

[4] (a) K. von Auwers, *Ann.*, **420**, 84 (1920); (b) L. H. Darling, A. K. Macbeth and J. A. Mills, *J. Chem. Soc.*, 1364 (1953); (c) S. Siegel, THIS JOURNAL, **75**, 1317 (1953); (d) W. E. Bachmann, A. Ross, A. S. Dreiding and P. A. S. Smith, *J. Org. Chem.*, **19**, 222 (1954); (e) F. R. Hewgill, P. R. Jefferies and A. K. Macbeth, *J. Chem. Soc.*, 699 (1954); (f) N. L. Allinger, *Experientia*, **10**, 328 (1954).

[5] (a) A. Skita, *Ber.*, **56**, 1014 (1923); (b) K. von Auwers and B. Ottens, *ibid.*, **57**, 437 (1924).

rule to which, within a precisely defined region of applicability, there would be no exceptions.[4b-f]

In the first paper in this series[4f] the physical properties of the *cis* and *trans* isomers of a great many compounds, including polysubstituted cyclohexanes and cyclopentanes, fused ring systems and olefins were examined, and these properties all seemed to be in agreement with the idea that the isomer of higher density, index of refraction, and boiling point was the less stable.[6] It was not clear at that time whether or not olefins were properly included with the other structures mentioned, since although a double bond is formally a two-membered ring, it is electronically quite different from the larger rings.[7] However, the experimental data available for monoölefinic hydrocarbons appeared without exception to fit the rule. On the other hand, at least one class of compounds, the α,β-unsaturated acids, were known not to be in agreement with the rule. For convenience in discussion, this rule will henceforth be referred to as the *conformational rule.* The existing forces of which this rule is a manifestation are not completely understood. Although the word steric has been used in this connection, it is clear that we are not here dealing with overlapping van der Waals radii, but rather with forces resulting from charge distribution between non-bonded atoms.[8] Whatever the nature of the forces involved, the existence of a conformational rule seems certain; it remains to state the rule correctly and define the region of its applicability.

It was suggested by van Arkel[9] that the boiling points of the *cis* and *trans* isomers of isomeric olefins were in fact determined by their dipole moments, both properties being greater for the same isomer.[10] For an olefin of the type ABC=CBA, where A and B are any substituents, the *cis* isomer would have the greater dipole moment, and consequently the higher boiling point. On the other hand, for an olefin of the type AHC=CHB, where A is any electron-attracting group and B is any electron-repelling group, the *trans* isomer has the greater dipole moment and, according to van Arkel's *dipole rule,* the higher boiling point. The dipole rule then predicts that with monoölefinic hydrocarbons the *cis* isomer will boil higher, but the reverse would be true with, for example, the α,β-unsaturated acid derivatives. These acid derivatives with their large dipole moments clearly obey the dipole rule, and they are in contrast to the predictions of the conformational rule. With the monoölefinic hydrocarbons the dipoles involved are quite small. With these compounds the same order of physical constants is predicted by both of the rules, and it is not certain which effect is in fact controlling the situation.

It seemed desirable at this point to disentangle the two rules by obtaining an isomeric pair of olefinic hydrocarbons in which the dipole rule and the conformational rule gave opposite predictions, so that the relative importance of these rules might be tested in a simple case. The *cis* and *trans* isomers of cyclodecene appeared to offer a suitable test case. Equilibrium studies appeared to indicate that the *cis* isomer had the lower free energy, and it also had the greater values of its physical constants, which facts suggested that perhaps in this case the dipole rule was the more important. However, there appeared to be some uncertainty as to just where the equilibrium point was for the reaction *trans*-cyclodecene $\rightleftarrows$ *cis*-cyclodecene. One of the earliest reported attempts at measurement of this equilibrium constant[11] indicated that $K < 1$ (at 175°), and this value was subsequently changed[12] to $\geqq 5.25$ (95°). Other workers have measured the value of this constant at various elevated temperatures,[13] and have indicated that it is "much greater" than 1. The temperatures at which the physical constants were measured were quite different from those at which the equilibrium constant was measured, the former being near room temperature. Inspection of models shows that the *cis* isomer has the greater entropy. Consequently, if the physical constants were related to the free energies, rather than the heat contents, none of the data mentioned above eliminates the possibility that the *cis* isomer has the more negative free energy at elevated temperatures, but that the free energies are reversed at room temperature because of the contribution of the entropy. There appears to be no reason to expect the physical constants to follow the free energies, either here or elsewhere, and in fact the data available in the literature are consistent only with the physical constants being related to the heat contents.[14] However, proof of the relationship appeared to be desirable in this case.

The dipole moments of the cyclodecenes could be calculated from bond moments. However, since the *trans* compound is obviously under some strain, the possibility that the normal planar sp^2 hybridization of the unsaturated carbons received a contribution from the tetrahedral sp^3 structure could not be dismissed. The latter type of hybridization, if it contributed to the actual structure of the molecule to any appreciable extent, would be expected to yield a very large dipole moment. Consequently the relative magnitudes of the dipole moments could not be unambiguously specified.

Results and Discussion

Pure samples of *cis*- and *trans*-cyclodecene were prepared by conventional methods, and their pu

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(6) Stable in this case refers to heat content rather than to free energy, but the distinction need be made only in certain rare cases.

(7) There is some evidence (M. T. Rogers and J. D. Roberts, THIS JOURNAL, **68**, 843 (1946); R. H. Eastman, *ibid.*, **76**, 4115 (1954)) that a three-membered ring is somewhere between a saturated and an unsaturated compound electronically, and what is concluded here for olefins may prove of importance also with cyclopropane derivatives.

(8) (a) E. N. Lassettre and L. B. Dean, Jr., *J. Chem. Phys.*, **16**, 151 (1948); **17**, 317 (1949); (b) N. W. Luft, *Trans. Faraday Soc.*, **49**, 118 (1953).

(9) A. E. van Arkel, *Rec. trav. chim.*, **51**, 1081 (1932); **52**, 719, 733 (1933); **53**, 91, 246 (1934).

(10) It was also pointed out by van Arkel that from Kopp's rule the isomer with the higher boiling point would also have the greater density. By definition the same isomer has the smaller molecular volume. It will also in general have the greater refractive index but the smaller molar refractivity.

(11) A. T. Blomquist, R. E. Burge, Jr., and A. C. Sucsy, THIS JOURNAL, **74**, 3636 (1952).

(12) A. T. Blomquist and A. Goldstein, *ibid.*, **77**, 1001 (1955).

(13) (a) V. Prelog, K. Schenker and H. H. Gunthard, *Helv. Chim. Acta*, **35**, 1598 (1952); (b) A. C. Cope, D. C. McLean and N. A. Nelson, THIS JOURNAL, **77**, 1628 (1955).

(14) N. L. Allinger, *J. Org. Chem.*, **21**, 915 (1956).

rity was established by a comparison of their physical properties, including infrared spectra, with the published values. The indications in the literature were that it might be rather difficult to establish equilibrium at room temperature within a reasonable length of time, consequently it was decided to measure the refractive index of the compounds at elevated temperatures. It was found that plots of the refractive indices of the two isomers as functions of temperature from 11–60° were exactly parallel, the values being larger for the *cis* isomer, which indicated that while these quantities might be related to the heat contents they did not appear to be related to the free energies.

A quantitative value of the equilibrium constant was desired at as low a temperature as possible. The published method of isomerization (*p*-toluenesulfonic acid) proved to be too slow to be practical at room temperature; thus pure samples of each of the two isomers were each isomerized to a mixture containing not more than 1% of the other isomer after 24 hours. Since the difficulty seemed to be the mutual insolubility of the acid and the olefin, sulfuric acid was substituted for the solid sulfonic acid. In this case the isomerization proceeded smoothly and cleanly, equilibrium appeared to be reached in less than 120 hours at 25°. The equilibrated mixtures obtained from both isomers under the same conditions were analyzed by the infrared method, and it was found that the mixtures were indistinguishable from the pure *cis* isomer. As little as 1% of the *trans* isomer readily could be measured, and 0.5% could be detected under the conditions used. The amount of *trans* isomer present in the equilibrium mixture was thus less than 0.5%. When the equilibration was carried out in this manner, there was no trace of side reactions such as decalin formation which hampered the earlier investigations. From the equilibration described it can be calculated that for the reaction (at 25°) *trans*-cyclodecene → *cis*-cyclodecene, $-\Delta F \geqq 3.1$ kcal. Consequently, according to the conformational rule the *trans* isomer should have the greater values for its physical properties.[15]

Lastly, the dipole moments of the *cis*- and *trans*-cyclodecenes were determined in heptane solution. The atomic polarizations were neglected in the calculations. If it is assumed that no error is introduced thereby, the dipole moment of the *trans* isomer is indistinguishable from zero, the experimental value being $0.15\ ^{+0.06}_{-0.17} \times 10^{-18}$ e.s.u. The *cis* isomer, on the other hand, with the same qualification as above, was found to have a dipole moment of $0.44 \pm 0.03 \times 10^{-18}$ e.s.u. These values support the assumption that the atomic polarizations may be neglected since these dipoles are "normal," and they also indicate the absence of any detectable amount of unusual hybridization. Thus the *dipole rule* predicts that the *cis* isomer will have the greater values of its physical constants.

It is clear in the present case that the dipole moments rather than the heat contents are reflected by the physical constants even though the difference in the former is nearly the smallest non-zero value that is to be found in stereoisomeric organic compounds, and the difference in the latter is as large as the difference found between most pairs of stereoisomers. Thus it appears that the conformational rule is applicable to isomers which do not differ in dipole moment, while for isomers which do so differ, the dipole rule is to be applied.

All unstrained saturated hydrocarbons necessarily have zero dipole moments,[16] and among these hydrocarbons the conformational rule should invariably apply. There are, to the author's knowledge, no exceptions among these compounds. The conformational rule should also apply to monofunctional compounds (*e.g.*, the 2-methylcyclohexanols) since the two isomers do not differ in dipole moment. With difunctional compounds the situation is less simple. The *cis*- and *trans*-1,2- and 1,3-disubstituted cyclohexanes (ee and ea conformations) have, to a first approximation, the same angles between substituents and should not differ in dipole moment, hence the conformational rule should apply. If the substituents are 1,4- and if either both are electron withdrawing or both are electron repelling, the *cis* isomer will have a greater dipole moment. The conformational rule then leads to the correct prediction here, but probably fortuitously. A 1,4-disubstituted cyclohexane with one electron-withdrawing group and one electron-attracting group will be another test case as the dipole and conformational rules lead to opposite predictions, and in this case the dipoles are physically separated. There appear to be no dipole moments reported for such a pair of isomers, and it is planned to make such measurements in the future.

It now appears desirable to state the conformational rule in a more precise way than was previously possible: *For stereoisomers in cyclic systems which do not differ in dipole moment, the isomer which has the smaller molecular volume is the isomer which has the higher heat content.*[17]

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Experimental

***trans*-Cyclodecene.**—Sebacoin was prepared from di-

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[15] Actually ΔH rather than ΔF should be used in this comparison (see ref. 14). Since the free energy change is so large, for ΔH to be opposite in sign from ΔF the entropy of the *cis* isomer would have to be greater than that of the *trans* by more than 11 e.u. This value is improbably large, and the use of ΔF in place of ΔH in this case seems justified. Subsequent to this work it was learned that the heats of hydrogenation of these compounds had been determined in the laboratories of Dr. R. B. Turner, and it was found that the *cis* isomer had the more negative heat content. The author wishes to thank Dr. Turner for making this data available in advance of publication.

[16] See the discussion by L. E. Sutton in E. A. Braude and F. C. Nachod, "Determination of Organic Structures by Physical Methods," Academic Press, Inc., New York, N. Y., 1955, p. 386.

[17] Several modifications have been incorporated in this statement of the rule relative to earlier versions,[4] and they require comment. First, the requirement of the same dipole moment seems clearly indicated by the present work. Second, the expression "smaller molecular volume" conveniently summarizes the nature of the densities, refractive indices, boiling points, molecular refractivities, and other less common properties (see ref. 4f for references to the experimental data). Lastly, the heat content is actually the quantity reflected in the physical properties. When the expression "relative stability" is used, there is some ambiguity as to whether heat content or free energy is indicated. It should be realized that for stereoisomers, differences in the latter are usually, but not necessarily, good approximations for differences in the former.

methyl sebacate[18] and was reduced with zinc and hydrochloric acid to cyclodecanone.[19] The ketone had $n^{25}\mathrm{D}$ 1.4802, reported[13b] $n^{20}\mathrm{D}$ 1.4800. The oxime of the ketone was prepared in 95% yield, m.p. 78.5–79.5°, reported[20] m.p. 80°. Reduction of the oxime with sodium and ethanol[20] gave cyclodecylamine in 63% yield, b.p. 101–103° (17 mm.), reported [13b] b.p. 84–86° (4 mm.). Cyclodecyl dimethylamine was obtained by methylation in 86% yield and was in turn converted to the trimethylammonium iodide (94%).[13b] The iodide was then converted to the hydroxide, which was decomposed at 100–130° (20 mm.).[11] The crude distillate was purified and redistilled at a bath temperature of 100–130° (20 mm.) to yield pure *trans*-cyclodecene, $n^{25}\mathrm{D}$ 1.4795, yield 71%. The reported constants are[11] $n^{20}\mathrm{D}$ 1.4822, b.p. 68–70° (10 mm.). The infrared spectrum of the compound proved to be identical with those reported.[11,13a]

***cis*-Cyclodecene.**—Sebacoin was oxidized to 1,2-cyclodecanedione with bismuth oxide[21] in 89% yield, m.p. 39.7–41.4°, reported[11] m.p. 40–41°. The diketone was converted to the acetylene by mercuric oxide oxidation of the dihydrazone.[11] The yield of pure cyclodecyne was 16%. The infrared spectrum of the compound was identical with that reported. Hydrogenation of the acetylene to the pure *cis*-olefin proceeded cleanly, the hydrogen uptake being quantitative. The catalyst used for the hydrogenation was described earlier.[22] The yield of *cis*-cyclodecene was 75%, distilled at a bath temperature of 100–130° (20 mm.), $n^{25}\mathrm{D}$ 1.4835. The reported[11] constants are $n^{20}\mathrm{D}$ 1.4854 and b.p. 194–195° (740 mm.). The infrared spectrum was identical with those published.[11,13a]

TABLE I

REFRACTIVE INDICES OF THE CYCLODECENES ($n\mathrm{D}$)

t, °C.	*cis*	*trans*	*t*, °C.	*cis*	*trans*
11.0	1.4892	1.4852	40.0	1.4769	1.4730
20.0	1.4856	1.4818	50.0	1.4728	1.4688
25.0	1.4835	1.4795	60.0	1.4686	1.4646
30.0	1.4811	1.4773			

The refractometer was calibrated before use. The values of the refractive indices found are in good agreement with those reported by Blomquist, Burge and Sucsy[11] (*cis* $n^{20}\mathrm{D}$ 1.4854, *trans* $n^{20}\mathrm{D}$ 1.4822), and that reported by Cope, McLean and Nelson[13b] (*trans* $n^{25}\mathrm{D}$ 1.4795), but these values differ significantly from the values reported by Prelog, Schenker and Günthard.[13a] Since this same deviation exists between the relative indices obtained by the latter group and the values obtained by others for other compounds and since it is consistent in both magnitude and direction, an instrumental error seems indicated.

Equilibration of the Cyclodecenes.—Three hundred milligrams of *trans*-cyclodecene and 20 mg. of concentrated sulfuric acid were allowed to stand at 25.0° for 120 hours with occasional shaking. The hydrocarbon layer was taken up in pure pentane, and the pentane layer was washed well with water. After removal of the solvent, the olefin was distilled at 20 mm. with a bath temperature of 100°. The same equilibration was then carried out starting with the *cis* isomer. The equilibrium mixtures were analyzed by the base line density infrared method,[12] using the pure *cis* and *trans* isomers as standards. It was found that the same mixture was obtained starting with either isomer, and it contained 97 ± 3% *cis* and not more than 0.5% *trans*. The equilibration experiments and analyses were then repeated as a check, and the results were identical.

Dipole Moments of the *cis*- and *trans*-Cyclodecenes.—The apparatus used for the dielectric constant measurements employed the heterodyne beat principle with a fixed frequency crystal oscillator at 100 kc. It has been described previously.[23] The dielectric constant cell held 60 ml. of solution and was thermostated in an oil-bath at 25.00 ± 0.02°. The general experimental procedure followed was that outlined by Smyth.[24] All weights were corrected to vacuum.

The molar polarization of the solute at infinite dilution was obtained following the method of Halverstadt and Kumler,[25] the pertinent relationship being

$$P_{2\infty} = [(\epsilon_1 - 1)/(\epsilon_1 + 2)][(1/d_1)][(M_2 - M_1\beta/d_1)] + [3M_1\alpha/(\epsilon_1 + 2)^2d_1]$$

where $\epsilon_{12} = \epsilon_1 + \alpha N_2$, $d_{12} = d_1 + \beta N_2$, ϵ_1 = dielectric constant of the solvent; d_1, N_1 and M_1 are, respectively, its density, mole fraction in solution and molecular weight while the quantities with subscripts 2 and 12 have the same significance for the solute and solution, respectively. The data are summarized in Table II.

TABLE II

DIELECTRIC CONSTANTS OF CYCLODECENE SOLUTIONS IN *n*-HEPTANE

cis			*trans*		
N_2	*d*	ϵ	N_2	*d*	ϵ
0.020228	0.68406	1.0986	0.020273	0.68394	1.9100
.020228	.68406	1.9081	.011876	.68224	1.9065
.011116	.68207	1.9041	.005392	.68080	1.9054
.005820	.68092	1.9021	.000000	.67963	1.9025
.003482	.68041	1.9007			
.000000	.67963	1.8991			

cis: $\alpha = 0.4596$, $\beta = 0.21844$, $P_{2\infty} = 49.35$ cc., $\epsilon_1 = 1.8992$, $d_1 = 0.67964$

trans: $\alpha = 0.328$, $\beta = 0.21330$, $P_{2\infty} = 45.89$ cc., $\epsilon_1 = 1.9028$, $d_1 = 0.67965$

The values of α and β were obtained in each case by the method of least squares. The calculation of the dipole moments from the molar polarizabilities made use of the Debye equation

$$\mu = 0.012181 \times 10^{-18}[(P_{2\infty} - R_{\mathrm{D}})T]^{1/2}$$

The molar refractivities were calculated from the refractive indices obtained in the present work (at 20°) and the densities reported by Blomquist and co-workers.[11] The values of *R* thus calculated are: *cis* 45.22, *trans* 45.43, which are in reasonable agreement with the theoretical value of 45.71.[26] The experimental rather than theoretical values for the molar refractivity were employed in the calculations, although use of the latter instead does not significantly affect the results.

The *trans* isomer was found to have a dipole moment of 0.15×10^{-18} e.s.u. The error in this value results almost entirely from the error in α, and it is estimated to be such that $\mu_{trans} = 0.15^{+0.06}_{-0.17} \times 10^{-18}$ e.s.u. The dipole moment of the *trans* isomer is hence indistinguishable from zero. For the *cis* isomer in a similar manner it is found that $\mu_{cis} = 0.44 \pm 0.03 \times 10^{-18}$ e.s.u.

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[18] N. L. Allinger, "Organic Syntheses," Vol. 36, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 79.

[19] A. C. Cope, J. W. Barthel and R. D. Smith, *ibid.*, p. 14.

[20] L. Ruzicka, M. Kobelt, O. Häfliger and V. Prelog, *Helv. Chim. Acta*, **32**, 544 (1949).

[21] W. Rigby, *J. Chem. Soc.*, 793 (1951).

[22] D. J. Cram and N. L. Allinger, THIS JOURNAL, **78**, 2518 (1956).

[23] (a) C. A. Brown and R. C. Osthoff, *ibid.*, **74**, 2340 (1952); (b) R. C. Osthoff, Ph.D. Thesis, Harvard University, 1951.

[24] C. P. Smyth in A. Weissberger's "Physical Methods of Organic Chemistry," Vol. I, Part II, Second Edition, Interscience Publishers, Inc., New York, N. Y., 1949, p. 1611.

[25] I. F. Halverstadt and W. D. Kumler, THIS JOURNAL, **64**, 2988 (1942).

[26] J. A. Leermakers and A. Weissberger, in H. Gilman's "Organic Chemistry," Vol. II, Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 1751.