The Molecular Structures of *trans*-2-Decalones. I. The Molecular Structure of *trans*-2-Decalone as Determined by Gas Phase Electron Diffraction[1]

George H. Pauli[2]

Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401. *Received April 5, 1968*

Abstract: The complete molecular structure of gaseous *trans*-2-decalone has been analyzed using the sector-microphotometer method of electron diffraction. The molecule was found to have both rings in the chair form. The average bond lengths were r_g(C–H) = 1.121 Å, r_g(C–O) = 1.225 Å, r_g(C–C) = 1.532 Å. The average bond angles were C–C–H = 109.5°, C–C–C = 111.3°, and C–C–C (carbonyl) = 114°. The parameters were determined by three independent analyses performed on three sets of photographic plates.

In recent years, Allinger has published a series of papers on the conformation of cyclohexanone rings, particularly as they are found in compounds with fused ring systems.[3] When diaxial dimethyl substituents are present, the ring is forced to distort drastically. In order to investigate such distortions in detail, it was decided to analyze the molecular structure of 1,1,10-trimethyl-*trans*-2-decalone, along with some decalones with fewer methyl groups, by gas phase electron diffraction. With compounds of this size there are so many possible internuclear distances that some assumptions must be made to analyze a structure from gas phase data. In order to see the effects of steric repulsions, a model which represents an undistorted decalone is helpful. Thus, as a comparison model of a relatively undistorted system, the structure of *trans*-2-decalone has been determined.

Experimental Procedure

Gas phase electron diffraction photographs of *trans*-2-decalone were taken on the Indiana University electron diffraction apparatus[4] using an r^3 sector. The photographs were recorded on 4 × 5 in. Kodak process plates using camera lengths of approximately 11 and 25 cm. The accelerating potential of the electron beam was 40 kV and the beam current was approximately 0.1 μA. The camera length and accelerating voltage were measured to a precision better than 0.05% in all cases. Blank photographs were also taken to determine the shape of extraneous (nonspecimen) scattering in the instrument. In order to obtain sufficient vapor pressure, the sample was heated to 110 ± 15° by immersing the sample bulb in an oil bath and heating the tube leading to the gas nozzle with an electrically insulated nichrome wire wrapped about the tube. The temperature of the gas nozzle was measured with a type J thermocouple. The absorbancies of three photographic plates from each camera length were measured on the Indiana University microphotometer.[4]

The sample was synthesized in this laboratory according to the procedure of Augustine.[5] No impurities could be detected by gas phase chromatography or infrared spectroscopy.

Treatment of the Data

It is convenient to convert the absorbancies of the photographic plates to leveled intensities before analyzing the structure. This conversion requires corrections for the extraneous scattering and for the use of the sector and a method of conversion from absorbancy to intensity. A correction for extraneous scattering was made to the absorbancy data by subtracting a function with the same shape as the extraneous scattering on a blank plate taken without gas in the system. This is not an optimum procedure but recent work indicates that the shape of the blank with gas in the system is the same except for the small angle region. Thus what is referred to here as extraneous scattering is more properly termed apparatus scattering as opposed to rest gas scattering. This function was obtained from a least-squares fit of the absorbancies of a blank plate for each camera distance using a low-order polynomial. (This required a quadratic equation for the 11-cm data and a cubic equation for the 25-cm data.) These functions were then subtracted from the absorbancies of the sample in the amount necessary to bring the leveled intensity at the outside edge of the plate to a value similar in magnitude to that in the middle, where apparatus scattering is small. A correction for the deviations of the sector from r^3 was obtained by taking the ratio of experimental to theoretical intensities for neon. All atomic scattering intensities were calculated using the elastic scattering factors of Strand and Bonham[6] and the inelastic scattering factors of Bewilogua.[7] These values are not the best currently available but are convenient to use and deviations between these values and more accurate values are smooth and may be absorbed in the background function. The sector correction was made using an average of the absorbancies of two neon plates taken at a camera length of 45 cm having similar exposure. Experiments with blank plates showed that at this camera length the apparatus scattering became small and was nearly constant across the plate. The electron intensity appeared to be linearly proportional to the absorbancy for all plates used. This was determined by comparing two 25-cm distance plates having a large exposure difference. The ratios of absorbancies of these two plates were constant at all points except for the effect of random noise; thus, the absorbancies were used directly as intensity values with no correction.[8a] Finally the intensities were leveled by

---

[1] The author wishes to thank the U. S. Public Health Service and the Petroleum Research Fund of the American Chemical Society for financial support of this work.

[2] Address inquiries to the Department of Chemistry, Lafayette College, Easton, Pa. 18042.

[3] N. L. Allinger, J. Allinger, and M. A. DaRooge, *J. Am. Chem. Soc.*, **86**, 4061 (1964).

[4] D. A. Kohl, Ph.D. Thesis, Department of Chemistry, Indiana University, Bloomington, Ind., 1967.

[5] R. L. Augustine, *J. Org. Chem.*, **23**, 1853 (1958).

[6] T. G. Strand and R. A. Bonham, *J. Chem. Phys.*, **40**, 1686 (1964).

[7] L. Bewilogua, *Physik Z.*, **32**, 740 (1931).

[8] (a) L. S. Bartell and L. O. Brockway, *J. Appl. Phys.*, **24**, 656 (1953). (b) Table I has been deposited as Document No. 10071 with

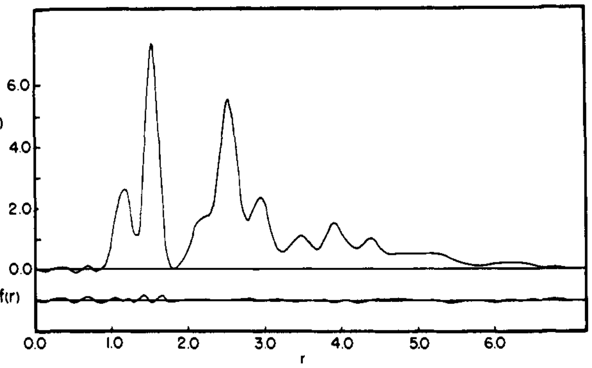

Figure 1. Experimental radial distribution curve obtained from set of data for *trans*-2-decalone. The lower curve is a plot of the difference between the experimental and calculated $f(r)$ curves.

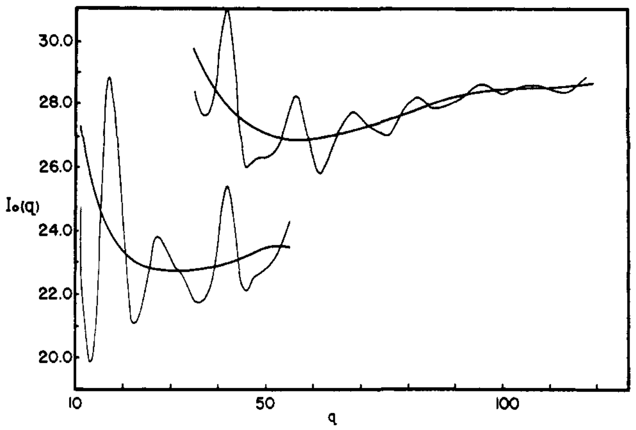

Figure 2. Experimental leveled intensity and background curves for *trans*-2-decalone obtained from one set of plates.

dividing by the atomic scattering. These leveled intensities, corrected for the sector and extraneous scattering, are given in Table I[8b] for three sets of plates.

Radial distribution curves were calculated from the intensities in the usual manner.[9] A damping factor was used to reduce the value of $M_c(q)$ to a tenth of its value at $q = 108$. A correction was made for nonnuclear scattering.[10] Experimental backgrounds were obtained as analytical functions described by six- or seven-term polynomials[11] refined according to the Karle nonnegative area criterion.[12]

In order to minimize bias from theoretical data at $q < 11$, a Fourier transformation of the experimental radial distribution curve was made and the $M_c(q)$ so obtained was used for the small angle scattering. This modification of the standard procedure did not appear to make a significant change in the radial distribution curve. Figure 1 shows the experimental radial distribution curve and the difference between it and a theoretical curve based on the best model. Figure 2 shows a leveled intensity curve and its experimental background for one set of plates.

In an experiment of this type it is extremely difficult to get realistic estimates of errors in the parameters measured. Therefore, following the suggestion of Morino, Kuchitsu, and Murata,[13] separate least-squares analyses were performed on radial distribution curves obtained from each of the three sets of plates. This should give an indication of the magnitude of uncertainties due to noise in the data or to any subjective steps in the data processing. The parameters agreed to better than ±0.005 Å for the more prominent bonded and shorter nonbonded distances (<2.5 Å). All internuclear distances not reported were calculated from a model compatible with the data and were held constant during the least-squares analysis. These consist of distances larger than 4 Å and nonbonded C–H, O–H, and H–H distances. The H–H distances have a negligible effect on the radial distribution curve and the small number of O–H nonbonded distances have only a small effect. Other than the major C–H nonbonded distance at 2.17 Å the C–H peaks are spread out across large regions of the radial distribution curve. Although there are several C–H peaks, they overlap each other and cannot be resolved. Their locations are known reasonably well from the framework structure of the carbons but their amplitudes remain quite uncertain. Since their positions were fixed during the analysis, the reproducibility obtained for distances larger than 2.7 Å will be better than the true uncertainty. Thus, although the reproducibility is good, it is doubtful that the bond lengths or amplitudes can be trusted to better than 0.02 Å for these longer distances.

Results

Table II gives the results of the least-squares analysis for the major peaks. In all cases the indices of resolution for both camera distances were larger than 0.9. The parameters reported are averages of the three analyses. The values for the distances and amplitudes must be considered to be averages of those distances of the same type within 0.1 Å of the listed value.

Table II. Bond Lengths and Amplitudes of Vibration for Major Internuclear Distances of *trans*-2-Decalone[a]

Bond	r_g, Å	l_g, Å
C–O	1.225	0.044
	2.402	0.063
	3.475	0.127
C–H	1.121	0.078
	2.176	0.113
C–C	1.532	0.053
	2.535	0.077
	2.971	0.084
	3.893	0.088

[a] The angles were CCC = 111.3°, CCH = 109.5°, and CCC(carbonyl) = 114°.

As would be expected, the data for nonbonded distances agree with a model having both rings in the chair form. Although small amounts of a skew boat cannot be ruled out, there is no evidence to support its presence.

---

the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington, D. C. 20540. A copy may be secured by citing the document number and by remitting \$1.25 for photoprints or \$1.25 for 35-mm microfilms. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

(9) R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, **31**, 702 (1959).

(10) L. S. Bartell, L. O. Brockway, and R. H. Schwendeman, *ibid.*, **23**, 1854 (1955).

(11) L. S. Bartell, D. A. Kohl, B. L. Carroll, and R. M. Gavin, Jr., *ibid.*, **42**, 3079 (1965).

(12) J. Karle and I. L. Karle, *ibid.*, **18**, 957 (1950).

(13) Y. Morino, K. Kuchitsu, and Y. Murata, *Acta Cryst.*, **18**, 549 (1965).

The most precisely determined parameter is the C–C bond length at 1.532 Å. This is usually thought of as an average of two types of bonds, the shorter sp^2–sp^3 bonds to the carbonyl carbon and the normal C–C bond. Although these two bonds cannot be resolved it is interesting to consider their effect on the average. A commonly accepted value for a C–C bond adjacent to a carbonyl bond is 1.50 Å,[14] although there is some evidence in favor of a slightly longer bond.[15] Any value for the C–C bond adjacent to the carbonyl bond which is less than 1.51 Å would require a value of 1.538 Å or more for the average C–C bond length for the other C–C bonds. This value is larger than that normally found in hydrocarbons but it is in agreement with that found for *trans*-decalin by Davis and Hassel.[16] This may be due to a general expansion of bond lengths in the double ring or to a longer C–C bond at the bridgehead.

The bonded C–H and C–O distances overlap in such a way that in order to obtain reasonable results, a value had to be assumed for the amplitude of vibration of the C–H bond. The results obtained for the bond lengths using the assumed amplitude agree with those obtained from other molecules with a carbonyl bond.[17]

Acknowledgments. The author wishes to thank Dr. Lao-Sou Su for doing the photographic development, and the Indiana University Research Computing Center for the use of their CDC-3600 digital computer. Thanks are also due to Professor Russell A. Bonham for his guidance in the work.

---

(14) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley and Sons, Inc., New York, N. Y., 1965, p 455.

(15) (a) A. Mossel and C. Romers, *Acta Cryst.*, 17, 1217 (1964); (b) R. Nelson and L. Pierce, *J. Mol. Spectry.*, 18, 344 (1965).

(16) M. I. Davis and O. Hassel, *Acta Chem. Scand.*, 18, 873 (1964).

(17) L. S. Bartell, J. P. Guillory, and A. T. Parks, *J. Phys. Chem.*, **69**, 3043 (1965).

The Structure of Sirenin[1a]

William H. Nutting,[1b] Henry Rapoport,[1b] and Leonard Machlis[1c]

Contribution from the Departments of Chemistry and Botany, University of California, Berkeley, California 94720.

Received May 24, 1968

Abstract: Sirenin (I) is the sperm attractant of the water mold *Allomyces*. Ozonolysis of its bis-NABS ester afforded NABS-hydroxyacetone in addition to two aldehydes (II and III), resulting from selective attack at each of the two double bonds. Structures for these aldehydes as well as for the dialdehyde IV obtained by treatment of sirenin with manganese dioxide were deduced from spectroscopic evidence. Oxidation of sirenin with periodate–permanganate led to the cyclopropane triester VI. Synthesis of this cyclopropane triester and three of its stereoisomers proved that sirenin was a sesquiterpene and possessed the carene bicyclic ring system. Additional comparison with *cis*- and *trans*-2-methyl-2-penten-1-ol allowed the stereochemistry and structure of sirenin to be established as 9-[(*E*)-4-hydroxy-3-methyl-2-butenyl]-10-hydroxy-2-carene.

The presence of hormones in the sexual reproduction of fungi was first suggested in 1880 but did not receive any experimental confirmation for another 40 years.[2] In 1958, the chemotactic hormone sirenin was first reported[3] and the presence of sexual hormones in other fungi has been demonstrated or postulated.[4] Our recent communication[5] provided the first complete structural characterization of a plant sex hormone, and a partial characterization of hormone A (antheridiol) has been reported.[6]

Sirenin is the sperm attractant produced by the female gametes of the water mold *Allomyces* and is active at concentrations of 10^{-10} *M*. The production, isolation, and characterization of sirenin and its 4-(4-nitrophenylazo)benzoate (NABS) esters have been described.[7] We now present evidence for the complete structure and stereochemistry of sirenin (I). It differs significantly from mammalian sex hormones in that sirenin is a sesquiterpene rather than a steroid.

Mass spectrometry and microanalyses[7] of sirenin and its derivatives established the molecular formula $C_{15}H_{24}O_2$ for sirenin. The formation of a diacetate and a bis-4-(4-nitrophenylazo)benzoate (NABS) ester (Ib) suggested that both oxygen functions in sirenin were alcohols which was further supported by ir absorption at 3600 cm^{-1}. That both hydroxyl groups were part of primary allylic alcohol moieties was indicated by the four-proton signal in the nmr spectrum at δ 3.97 which shifted to 4.75 in Ib. From the magnitude of the shifts of the vinyl proton signals at δ 5.38 and 5.80 in I to 5.59 and 5.98 in Ib, respectively, two primary allylic alcohols with a β-vinyl proton were postulated since the carbinol proton signal was unsplit. One tertiary and one vinyl methyl group in sirenin were also indicated by the singlets at δ 0.88 and 1.67, respectively.

In order to elucidate the nature of the double bonds, bis-NABS-sirenin (Ib) was partially ozonized. In

---

(1) (a) Support in part by the National Science Foundation is gratefully acknowledged; (b) Department of Chemistry; (c) Department of Botany.

(2) J. R. Raper, *Amer. J. Bot.*, 47, 794 (1960).

(3) L. Machlis, *Physiol. Plant.*, **11**, 181 (1958).

(4) L. Machlis in "The Fungi," Vol. 2, G. C. Ainsworth and A. S. Sussman, Ed., Academic Press, New York, N. Y., 1966, Chapter 13.

(5) L. Machlis, W. H. Nutting, and H. Rapoport, *J. Amer. Chem. Soc.*, **90**, 1674 (1968).

(6) T. C. McMorris and A. W. Barksdale, *Nature*, **215**, 320 (1967).

(7) L. Machlis, W. H. Nutting, M. W. Williams, and H. Rapoport, *Biochemistry*, **5**, 2147 (1966).