

TABLE I
 ESTERS OF 4-CHLORO-19-NORTTESTOSTERONE (III)

No.	R	M.P.	Yield, % ^a	Recryst. Solv.	Formula	Analyses			
						Calcd.		Found	
						C	H	C	H
1	CH ₂ (CH ₂) ₆	Oil	13	^b	C ₂₆ H ₃₇ O ₃ Cl	71.32	8.86	71.48	9.19
2	CH ₂ (CH ₂) ₃ CH—CH ₂ —CH ₂ ^c	88–89	17	Et ₂ O-PE ^d	C ₂₆ H ₃₇ O ₃ Cl	72.11	8.61	72.27	8.70
3	C ₆ H ₅ CH ₂ CH ₂	127–130	17	Et ₂ O ^e	C ₂₇ H ₃₅ O ₃ Cl	73.53	7.54	73.39	7.77
4	<i>p</i> -ClC ₆ H ₄ OCH ₂ ^f	167–168	37	MeCOEt	C ₂₆ H ₃₀ O ₄ Cl ₂	65.41	6.33	65.28	6.37
5	C ₆ H ₅	192–196	12	Et ₂ O ^g	C ₂₆ H ₂₉ O ₃ Cl	72.71	7.08	72.47	7.37

^a Yields are of pure product based on 19-nortestosterone. ^b Eluted by benzene and 1:1 benzene-ether. ^c B. Camerino, B. Patelli, and A. Vercellone, *J. Am. Chem. Soc.*, **28**, 3540 (1956) disclosed the biological activity of this compound but not the physical properties. ^d Eluted by 1:1 benzene-ether. ^e Eluted by 1:1 petroleum ether-benzene and benzene. ^f $[\alpha]_D^{25} +60.5^\circ$ (1% in chloroform). ^g Decolorized by passage through alumina in benzene.

4-Chloro-19-nortestosterone-17 β -benzoate (Table I, No. 5). The preparation of this substance differed from the other esters in that 19-nortestosterone-17 β -benzoate⁸ was epoxidized using the same general procedure as for 19-nortestosterone. The remainder of the sequence was unchanged.

Isolation of estradiol 17 β -heptanoate. The preparation of 4-chloro-19-nortestosterone-17 β -heptanoate, starting from 10.0 g. (0.0366 mole) of 19-nortestosterone was carried out as described above. The total crude final product was chromatographed on 770 g. of ethyl acetate washed alumina. After elution of the desired oily ester with a total of 5000 ml. of petroleum ether, benzene and ether mixtures, the estradiol ester was eluted by 1:1 benzene:ether and ether and recrystallized from ligroin to give 2.35 g. (18% from 19-nortestosterone) of colorless plates, m.p. 94–96° (lit.⁹ 96–98°), $\epsilon_{281}^{C_2H_5OH}$ 2000 (shoulder at 286 m μ), μ^{Nujol} 2.9, 5.9, 6.2, 6.3, 6.7, 7.8, 8.1, 8.7, 11.5, 12.3, 12.8.

Anal. Calcd. for C₂₅H₃₆O₃: C, 78.08; H, 9.44; mol. wt. 384. Found: C, 78.21; H, 9.64; mol. wt. 370 (camphor).

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(8) L. Hicks, U. S. Patent 2,698,855 (Jan. 4, 1955). Through *Chem. Abstr.*, **49**, 7009 (1955).

(9) K. Junkmann, *Arch. exp. Path. Pharmacol.*, **220**, 358 (1953).

The Dipole Moment of Norbornylene. Use of the IBM 650 Computer for Dipole Moment Calculations¹

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Norbornylene (bicyclo[2.2.1]hept-2-ene) is known to contain a "strained" olefinic linkage by the usual chemical test of phenyl azide addition.² A comparison of the infrared spectrum of norbornylene³ with other *cis* olefins⁴ showed the olefinic

(1) This work was supported by a grant from the Sloan Foundation.

(2) J. H. Boyer and F. C. Canter, *Chem. Revs.*, **54**, 1 (1954).

(3) P. von R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **78**, 5702 (1956).

(4) N. Sheppard and D. M. Simpson, *Quart. Rev.*, **6**, 1 (1952).

hydrogen stretching band of the former at 3070 cm.⁻¹, considerably higher than the usual value (3010 cm.⁻¹). It was shown that the corresponding absorption was found at 3000 cm.⁻¹ for *trans*-cyclooctene, another strained olefin, which indicated the strain in this case was quite different from that found in norbornylene.⁵ The dipole moment of *trans*-cyclooctene was found to have the unusually large value of 0.8 D, and a unique strained geometry about the double bond was proposed⁵ to account for this large moment.

TABLE I
INFRARED ABSORPTION MAXIMA, CM.⁻¹

	=C—H	C=C
<i>cis</i> -4-Octene	3010	1650
<i>cis</i> -Cyclooctene	3010	1664
<i>trans</i> -Cyclooctene	3000	1658
Cyclohexene	3020	1650
Norbornylene	3070	1575
1-Butyne	3300	—

Norbornylene is strained in quite a different way from *trans*-cyclooctene as is indicated by the infrared spectrum. Some pertinent infrared data are summarized in Table I. In norbornylene, the C—C=C bond angles are reduced below the preferred value of 120° by the geometrical requirements of the ring system. There is a consequent increase in the *p* character in the C—C bonds of the olefinic system, and a corresponding increase in *s* character in the olefinic C—H bond. These effects increase the =C—H stretching frequency considerably, and simultaneously reduce the C=C stretching frequency. A quantitative relationship exists⁶ between the C—H stretching frequency and the amount of *s* character in the bond, and from the position of the norbornylene band relative to the corresponding bands in an ordinary *cis* olefin and a terminal acetylene (Table I), the appreciable strain is apparent.

(5) N. L. Allinger, *J. Am. Chem. Soc.*, **80**, 1953 (1958).

(6) C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

It was of interest to determine what effect the type of strain present in norbornylene exerted upon the dipole moment. The moment was therefore measured in the customary way in heptane solution, and it was found to have the value of 0.40 D. This value may be compared with those found for the ordinary *cis* olefins cyclooctene⁵ (0.43 D) and cyclodecene⁷ (0.44 D). Clearly the strain in the norbornylene case, which although considerable in terms of energy,⁸ is inconsequential in its effect on the dipole moment.

The calculation of a dipole moment from dielectric constant measurements is a tedious process with a desk calculator. If six or seven experimental measurements are taken, the whole calculation, including rechecking and correcting of errors requires the better part of a day. We have therefore applied automatic computing methods, utilizing an IBM 650 computer, to the solution of this problem. Large digital computers of this general class are now rather generally available, and are ideally suited to solving lengthy problems of this kind. Advances in automatic programming made in the last few years now make it possible for the average chemist to program and use such a computer with much less difficulty than is commonly supposed. The program was first prepared and checked by calculating known moments from available data. To calculate a dipole moment now that the program is available, the experimental data (weights, dielectric constants, *etc.*) are put directly onto punched cards, which takes about 15 min. The computer is then able to read the program and data cards, do the calculations, including the two least squares fittings, and punch out all of the desired data (N_2 , $d_{1,2}$, $\epsilon_{1,2}$, $P_{2\infty}$, and μ) in about 3 min.

EXPERIMENTAL

Materials. The norbornylene (obtained from the reaction of ethylene with dicyclopentadiene⁹) was redistilled before use, b.p. 97°, m.p. 44.0–44.5° (sealed capillary). The heptane solvent was purified as described earlier.⁸ The apparatus used for the dielectric constant measurements has been described.¹⁰

Calculations. The general procedure of Halverstadt and Kumler¹¹ as described earlier⁷ was used as the basis for the program. The program was initially written in the RUNCIBLE¹² language. This program was translated by RUNCIBLE into the SOAP¹³ input program, which was in turn converted by SOAP to the machine language program in the usual way.¹⁴

(7) N. L. Allinger, *J. Am. Chem. Soc.*, **79**, 3443 (1957).

(8) R. B. Turner, W. R. Meador, and R. E. Winkler, *J. Am. Chem. Soc.*, **79**, 4116 (1957).

(9) J. Meinwald and N. J. Hudak, *Org. Syntheses*, **37**, 65 (1957).

(10) M. T. Rogers, *J. Am. Chem. Soc.*, **77**, 3681 (1955).

(11) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(12) "Revised Unified New Compiler with IT Basic Language Extended."

(13) "Standard Optimum Assembly Program."

(14) RUNCIBLE I, Computing Center, Case Institute of Technology, Cleveland, Ohio, 1958.

The actual experimental data, the weight of the empty flask, flask plus sample, flask plus sample plus solvent, cell constant, condenser correction, absolute temperature, and so on were placed on punched cards. The program and data were then run into the computer. The program instructed the computer to read the data and calculate N_2 , $d_{1,2}$, and $\epsilon_{1,2}$ and then calculate from these quantities d_1 , ϵ_1 , α and β by the method of least squares. After these least squares lines were available, the computer continued by testing the experimental points against the least squares lines and it would have discarded any point which was further from the line than an amount δ .

A new line would then have been calculated omitting these discarded points. The value of δ was introduced into the computer as data, and so may be varied from one calculation to the next. In this particular case the points were all within 0.0002 in mole fraction of the N_2 vs. $d_{1,2}$ line and within 0.0004 in dielectric constant of the $\epsilon_{1,2}$ vs. N_2 line, hence none were discarded. The probable error in the moment is estimated at 0.05 D. The computer then continued by calculating A, B, and C, and then $P_{2\infty}$. The molar refractivity, calculated by hand from tables,¹⁵ was inserted into the computer with the data. (Atomic polarization was neglected. In other cases it could be inserted with the molar refractivity if desired.) The moment was then calculated, and all of the desired quantities were punched by the computer as output. The output data are listed in Table II.

TABLE II
DIPOLE MOMENT DATA FOR NORBORNYLENE IN HEPTANE
AT 25°C.

N_2	$d_{1,2}$	$\epsilon_{1,2}$
0.0239207	0.680836	1.9141
0.0201392	0.680294	1.9126
0.0144320	0.679471	1.9117
0.0101019	0.678902	1.9099
0.0026978	0.677821	1.9081
0.0000000	0.677423	1.9077
$\alpha = 0.26746$	$\beta = 0.14122$	$\epsilon_{1,2} = 1.9075$
$d_1 = 0.677447$	$P_{2\infty} = 32.889$	$\mu = 0.398D$

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(15) J. A. Leermakers and A. Weissberger, in H. Gilman, "Organic Chemistry," Vol. II, Second Ed., John Wiley and Sons, Inc., New York, N. Y., 1947, p. 1751.

Identity of Compound A from Kava Root with 5,6-Dehydrokavain

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We established the structure 4-methoxy-6-(β -styryl)- α -pyrone for a compound isolated from the