[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY
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The Dipole Moments of Androstan-17-one, Testan-11-one, and Testane-11,17-dione

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The dipole moments of androstan-17-one, testan-11-one, and of testane-11,17-dione derived from dielectric constant measurements of benzene solutions of these compounds at 25° are, respectively, 3.0, 3.0, and 4.1 *D*. The result obtained for testane-11,17-dione is significantly lower than the value of 4.6 *D* calculated for this substance, a discrepancy which is suggestive of an interaction between the two carbonyl groups, postulated previously for 11,17-diketosteroids on the basis of infrared evidence only.

In 1949 Jones, Humphries, and Dobriner[1] observed that the infrared absorption maximum associated with the 17-carbonyl group in 17-ketosteroids is displaced from its normal position (1742–1745 cm.$^{-1}$) to 1748–1754 cm.$^{-1}$ in compounds possessing both an 11- and a 17- carbonyl function. Similar displacements have been observed in 21-acetoxy-20-ketosteroids[1,2] and in 12α- and 12β-acetoxy-11-ketosteroids[3] but not in the structurally related 17β-acetoxy-16-keto derivatives.[4] Although the origins of these shifts are not clearly understood, the suggestion has been made that they result from the interaction of dipolar functions that are proximate in space through a direct field effect.[4,5] This suggestion has prompted us to search for anomalies in the dipole moment of testane-11,17-dione (III) in which the relative position of the two carbonyl groups is fixed by their incorporation in a rigid ring system.

EXPERIMENTAL

The dielectric constants of benzene solutions (25°) of androstan-17-one, testan-11-one, and testane-11,17-dione were determined at 200 kc./sec. using the same capacitance-conductance bridge, test cell, and circuit as employed previously.[6]

Materials. The benzene used in the present work was purified by the method of the previous investigation.[6]

Androstan-17-one. 3β-Benzoyloxyandrostan-17-one[7] (2.2 g. m.p. 220–221°) was pyrolyzed under reduced pressure at 420° for 0.5 hr. The resulting material was taken up in ether, washed with dilute sodium hydroxide, and evaporated to dryness. Separation of the olefinic product from unchanged starting material was accomplished by treatment with methanolic potassium hydroxide, followed by filtration of a petroleum ether solution of the hydrolysate through alumina. Hydrogenation of the crude unsaturated ketone over platinum and subsequent oxidation with chromium trioxide furnished 603 mg. of androstan-17-one, m.p. 118–119°. A pure product, m.p. 121–122°,[8] $\nu_{max}^{CS_2}$ 1745 cm.$^{-1}$, was obtained by recrystallization from aqueous methanol.

Testan-11-one. A mixture of 820 mg. of testane-11,17-dione (prepared as described below), 1.5 g. of potassium hydroxide, 0.5 ml. of 85% hydrazine, and 15 ml. of diethyleneglycol was heated under a reflux condenser at 170° for 0.5 hr. The condenser was then removed and the temperature was allowed to rise to 200°, where it was maintained for a period of 2 hr. The product was isolated by ether extraction and crystallization from aqueous methanol; 403 mg., m.p. 115.5–118.5°. Several recrystallizations from aqueous methanol afforded a pure sample melting at 119–120°, $\nu_{max}^{CS_2}$ 1713 cm.$^{-1}$

Anal. Calcd. for $C_{19}H_{30}O$: C, 83.15; H, 11.02. Found: C, 82.99; H, 11.10.

Testane-11,17-dione. 3α-Hydroxytestane-11,17-dione (3.0 g., m.p. 187–188°)[9] was converted into the corresponding benzoate (3.6 g., m.p. 223–225°) by treatment with benzoyl chloride and pyridine. Three recrystallizations from methylene chloride–petroleum ether (b.p. 30–60°) afforded the analytical sample, m.p. 226–227°.

Anal. Calcd. for $C_{26}H_{32}O_4$: C, 76.44; H, 7.90. Found: C, 76.29; H, 8.02.

Pyrolysis of the benzoate was carried out under reduced pressure at 400° for 1 hr. The resulting product was hydrogenated over palladized charcoal in a mixture of ethanol and benzene and yielded 1.5 g. of testane-11,17-dione meltat 139–142°. The analytical sample, m.p. 144–145°, $\nu_{max}^{CS_2}$ 1716, 1751 cm.$^{-1}$, was obtained after two recrystallizations from aqueous methanol.

Anal. Calcd. for $C_{19}H_{28}O_2$: C, 79.12; H, 9.79. Found: C, 79.06; H, 9.91.

RESULTS AND DISCUSSION

For the dilute solutions studied both the density change, Δd, and the dielectric constant increment, $\Delta\epsilon$, were proportional to the weight per cent solute, W, within experimental error. The average values of $\Delta\epsilon/W$ and $\Delta d/W$ were used to calculate the solute polarization, P_2, and the dipole moment,

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(1) R. N. Jones, P. Humphries, and K. Dobriner, *J. Am. Chem. Soc.*, **71**, 242 (1949).

(2) R. N. Jones, V. Z. Williams, M. J. Whalen, and K. Dobriner, *J. Am. Chem. Soc.*, **70**, 2030 (1948); R. N. Jones, P. Humphries, F. Herling, and K. Dobriner, *J. Am. Chem. Soc.*, **74**, 2820 (1952).

(3) D. H. W. Dickson and J. E. Page, *J. Chem. Soc.*, 447 (1955).

(4) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 861 (1957).

(5) R. N. Jones and C. Sandorfy, *Techniques of Organic Chemistry*, IX, "Chemical Aspects of Spectroscopy," ed. A. Weissberger, Interscience Publishers (1956), pp. 462–498.

(6) H. R. Nace and R. B. Turner, *J. Am. Chem. Soc.*, **75**, 4063 (1953).

(7) L. Ruzicka, M. W. Goldberg, and J. Meyer, *Helv. Chim. Acta*, **18**, 210 (1935).

(8) A. Butenandt and H. Dannenbaum, *Z. physiol. Chem.*, **229**, 192 (1934).

(9) Supplied through the courtesy of Dr. E. B. Hershberg, Schering Corp.

μ, from the relations employed previously.[6] The solute electronic polarization, $P_{E2} = 81.2$, calculated by Kumler,[10] for androstane-3,17-dione was used for testane-11,17-dione, and a value of $P_{E2} = 81.2$ for androstan-17-one and for testan-11-one was derived from the group refractions given by Smyth.[11] Measured solution dielectric constants, ϵ_{12}, densities, d_{12}, and weight per cent values, W, are listed in Table I.

TABLE I

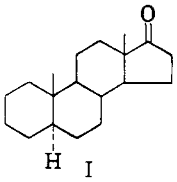
MEASUREMENTS IN BENZENE AT 25°

W	ϵ_{12}	d_{12}
	Androstan-17-one	
1.2013	2.315	0.8738
0.7658	2.301	0.8740
0.5884	2.292	0.8738
0.3199	2.283	0.8726
	Testan-11-one	
1.1573	2.311	0.8741
0.9072	2.307	0.8740
0.7146	2.299	0.8738
0.3329	2.283	0.8722
	Testan-11,17-dione	
1.1473	2.363	0.8751
0.8705	2.324	0.8742
0.7048	2.315	0.8738
0.3952	2.298	0.8732

The values obtained for the dipole moments of the various compounds were: for androstan-17-one (I), 3.0 *D;* for testan-11-one (II), 3.0 *D;* and for testane-11,17-dione (III), 4.1 *D*. For purposes of comparison with the experimental result, the theoretical dipole moment of testan-11,17-dione was calculated as follows. The values of 3.0 *D* obtained for androstan-17-one and for testan-11-one were assumed for the individual moments of the two carbonyl functions in the dione (III), and the angle φ between these groups was derived by measurement of the direction cosines of the carbon-oxygen bonds in a carefully constructed Barton model[12] of testan-11,17-dione, which was mounted in a fixed position with respect to the coordinate system. Use of the relation

$$\cos \varphi = \cos \alpha_1 \cos \alpha_2 + \cos \beta_1 \cos \beta_2 + \cos \gamma_1 \cos \gamma_2$$

gave a value of 81.5° for φ, and the resultant moment calculated for testane-11,17-dione was 4.6 *D*. The discrepancy of 0.5 units between this value and the experimental quantity lies outside the limits of error of the method and provides independent evidence for the interaction theory, which hitherto has been supported by spectroscopic data only.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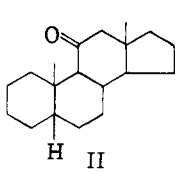
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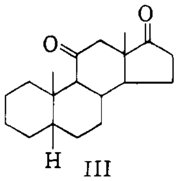
III

The precise nature of the phenomenon is, of course, not defined by the dipole moment results. It may involve mutual suppression of polar contributions to the hybrid structures of the carbonyl groups through the field effect, or alternatively an expansion of the carbonyl-carbonyl angle (φ) by dipolar repulsion.[13] The possibility that strains set up by the incorporation of two trigonal carbon atoms in the *trans*-fused C/D ring system may also be involved cannot be dismissed. It is especially worthy of note, however, that both spectroscopic and dipole moment anomalies of appreciable magnitude are observed in a system possessing 1,4-dicarbonyl groups that are nearly orthogonal and in which dipolar interactions should hence be minimal.

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[10] W. D. Kumler, *J. Am. Chem. Soc.*, **67**, 1901 (1945).

[11] C. P. Smyth, *Dielectric Constants and Molecular Structure*, Chemical Catalog Co. (Reinhold Publishing Corp.), New York, N. Y (1931).

[12] D. H. R. Barton, *Chemistry and Industry*, 1136 (1956).

[13] The value calculated for φ from the observed moments of androstan-17-one, testan-11-one, and testane-11,17-dione is 90.4° as compared with 81.5° obtained from the model.