Radical Addition of Thiophenol to Bicyclo[2.2.2]oct-2-ene (III).—Employing a procedure similar to that of Cristol and Brindell,[28] an equimolar quantity of freshly distilled thiophenol was added to 4.0 g. (0.037 mole) of III. Distillation of the reaction mixture gave 5.53 g. (68%) of 2-thiophenylbicyclo[2.2.2]octane, b.p. 118–122° (0.8 mm.), $n^{25}\text{D}$ 1.5859. A portion of this material was redistilled for analysis, b.p. 113.4–114° (0.6 mm.), $n^{25}\text{D}$ 1.5851. The infrared spectrum (capillary) shows the following bands in the fingerprint region: 1270(m), 1200(w), 1093(m), 1067(w), 1027(m), 961(w), 742(s) (doublet) and 695(s) (doublet) cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{18}S$: C, 77.00; H, 8.31; S, 14.69. Found: C, 77.25; H, 8.33; S, 14.91.

Desulfurization of 2-Thiophenylbicyclo[2.2.2]octane.—Approximately 5 g. of Raney nickel was added to a solution of the thioether (600 mg., 2.75 mmoles) in 40 ml. of 95% ethanol. The mixture was refluxed for 48 hr. The catalyst was removed by filtration and the filtrate was added to 300 ml. of water. This aqueous solution was then extracted with several portions of pentane and the combined extracts were washed with water, dried and concentrated by distillation. Sublimation of the residue afforded 124 mg. (41%) of bicyclo[2.2.2]octane, m.p. 166–168.5°, m.m.p. 166–169°. The infrared spectrum of this product shows none of the bands characteristic of bicyclo[3.2.1]octane.

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[28] S. J. Cristol and G. D. Brindell, *J. Am. Chem. Soc.*, **76**, 5699 (1954).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNA.]

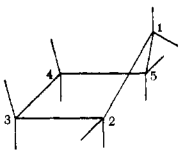
The Conformations of Substituted Cyclopentanes. II. Maximally Puckered Envelope and Half-chair Models for Fused Ring Systems[1]

BY FREDERICK V. BRUTCHER, JR., AND WILLIAM BAUER, JR.[2]

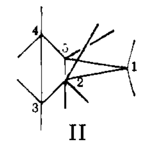
RECEIVED AUGUST 30, 1961

A pair of maximally puckered envelope and half-chair models ($\theta = 60°$) for use in the description of conformations of highly substituted and ring fused cyclopentanes is presented. Their bond bending energies (V_B), torsional energies (V_t) and electron correlation energies (London forces, E_c) have been calculated for comparison purposes. The use of these models in the estimation of the relative stabilities of the envelope and half-chair conformation of given molecules is discussed.

In a previous paper,[3] the two important conformations, the envelope (I) and half-chair (II) were described and applied to simply substituted, monocyclic cyclopentanes. In order to utilize these conformations in fused ring systems, however, models must be constructed in which the projected angle, $\theta_{1,2}$, sighted along C_1–C_2 in I or $\theta_{3,4}$ in II will be 60°.[4–6] The Pitzer and Donath model for cyclopentane itself has $\theta_{1,2} = \theta_{5,1} = 46.1°$ for the envelope conformation and $\theta_{3,4} = 48.1°$ for the half-chair.[4] Further, our earlier model for cyclopentanone was mainly concerned with the projected angle between the carbonyl group and the α-substituent.[3] In this paper, we have constructed through vector analytical techniques[4,7,8] a pair of maximally puckered models of general applicability to fused rings and highly substituted cyclopentanes.

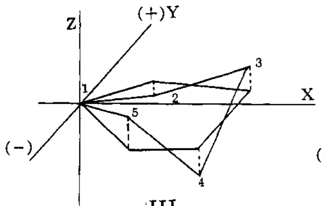


I

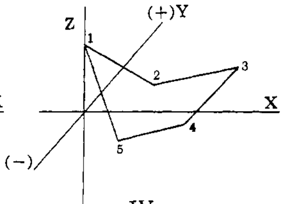


II

We begin with a planar, five-membered ring located in a coördinate system as shown below (III). The amplitude of puckering (q)[4,9] was allowed to increase until the torsional angles (θ's) had in each form reached the desired values. The interior angles of the ring (ω_i) and torsional angles (θ_{ij}) for the resulting, symmetrical models are given in Table I.[10]



III



IV

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[1] Previous communication in this series, F. V. Brutcher, Jr., and William Bauer, Jr., *Science*, **132**, 1489 (1960). The material in this paper and the following one on ring D in the steroids was presented at the Autumn Meeting of the National Academy of Sciences held at the University of Pennsylvania on November 14, 1960.

[2] Armstrong Cork Co. Predoctoral Fellow 1960–1961.

[3] F. V. Brutcher, Jr., T. Roberts, S. J. Barr and N. Pearson, *J. Am. Chem. Soc.*, **81**, 4915 (1959).

[4] K. S. Pitzer and W. E. Donath, *ibid.*, **81**, 3213 (1959).

[5] Inspection of scale models of steroid rings C and D built according to the reported X-ray analyses of several steroid systemsi ndicates that this is approximately the case.[6] The much more complicated fused ring cases, where θ may not be equal to 60°, are under consideration in this Laboratory.

[6] (a) C. H. Carlisle and D. Crowfoot, *Proc. Royal Soc.* (*London*), **184A**, 81 (1945); (b) D. Crowfoot, Hodgkin and D. Sayre, *J. Chem. Soc.*, 4561 (1952); (c) R. G. Curtis, J. Friedrichsons and A. McL. Mathieson, *Nature*, **170**, 321 (1952); *J. Chem. Soc.*, 2159 (1953).

[7] The treatment involves the assumption that the angles $\omega_2 = \omega_5$ are also equal to ω_1. This assumption, which makes the calculations tractable; was found by Kilpatrick, Pitzer and Spitzer[8] to give substantially the lowest energy.

[8] J. E. Kilpatrick, K. S. Pitzer and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 211 (1947).

[9] It is important to note that q in Å., which is a *measure* of the amplitude of puckering, is *not* the distance of carbon 1 in the envelope out of the C_2–C_3–C_4–C_5 plane. We have transformed q for cyclopentane itself and also for our maximally puckered models to the following numbers which are more meaningful for organic chemists. In cyclopentane itself the C_1 distance (envelope) from the C_2–C_3–C_4–C_5 plane is 0.75 Å.; in our maximally puckered model it is 0.91 Å. For the half-chair with C_2–C_1–C_5 the reference plane, C_3 in cyclopentane itself is 0.39 Å. above the reference plane while C_4 is equally below the plane. In our maximally puckered model (half-chair) C_3 is 0.48 Å. above and C_4 is 0.48 Å. below the C_2–C_1–C_5 plane. It also might be pointed out that q is not needed for vector analytical work on organic molecules (*e.g.*, for cyclohexene see E. J. Corey and R. A. Sneen, *ibid.*, **77**, 2505 (1954) and for bicycloheptane, C. F. Wilcox, *ibid.*, **82**, 414 (1960)). The technique involving q is derived from vibrational methods of analysis such as those used for pseudorotating molecules such as cyclopentane.[8]

[10] It is useful to note that when a cyclopentane ring adopts either the envelope or half-chair *all* interior angles turn out to be *less* than the tetrahedral value of 109° 28′.

TABLE I

Angle	Envelope (q = 0.633 Å.)	Half-chair (q = 0.615 Å.)
$\omega_1 = \omega_2 = \omega_5$	96.6°	103.0°
$\omega_3 = \omega_4$	104.3°	95.9°
$\theta_{1,2} = \theta_{5,1}$	60.0°	19.0°
$\theta_{2.3} = \theta_{4.5}$	36.5°	50.0°
$\theta_{3.4}$	0.0°	60.0°

It is interesting to observe that while the envelope has two fully staggered ethanes as compared to the one possessed by the half-chair, its remaining positions are relatively more eclipsed than those of the half-chair with the net result that the total torsional energies are essentially identical (see Table II). Further, it is of prime interest to call attention to the intriguing strain energy distribution about the cyclopentane ring. It is apparent that any carbon atom of the ring whose C–H bonds are under intense torsional stress is at the same time a region of least bond-bending deformation. Thus in the envelope, the interior angle of carbon 1, ω_1, is highly deformed (96.6°), but carbon 1 has a staggered arrangement of its remaining valence bonds. In the envelope, carbon 3 has a high torsion energy with one eclipsed and one partially eclipsed ethane-like interaction, but it has a minimal stress due to bond-bending (ω_3 = 104.3°). The same considerations apply to the half-chair and lead one to conclude that the strain energy of puckering in cyclopentane is not borne too unequally by any one carbon atom in the ring, but rather is well distributed around the entire system. It is this smooth distribution that permits pseudorotation and the destruction of such distribution on substitution that allows one or the other of these conformations to be favored in cyclopentane derivatives.

TABLE II

ENERGIES OF THE MAXIMALLY PUCKERED CYCLOPENTANES

Energy contribution	Envelope	Half-chair
Bond bending V_B	9.68	8.69
Torsion V_t	4.66	4.70
Zero point vibration	85.26	85.26
Electron correlation (E_c)	−47.95	−47.29
Bond formation	−59.0	−59.0
Heat of formation H_0^0	−7.35	−7.64
H_0^0 at q = 0.5[a]	−9.02	(q 0.48[a]) −8.49

[a] The heats of formation of cyclopentane itself, as given by Pitzer and Donath.

It is now necessary to employ the above models in detailed calculations of their energy content. It is apparent that where appropriate force constants (k) for bond bending and potential barriers to rotation (V_0) are available from simpler systems, one can estimate the bond bending (V_B) and torsional energies (V_T) of the possible conformations of a given molecule from the standard eq. i and ii. The values for ω_0 are here taken as 109.5° and 116.3° (CCC bond angles in acetone)[11] for tetrahedral

$$V_B = k/2\,(\omega_0 - \omega)^2 \qquad \text{i}$$

$$V_T = V_0/2\,(1 + \cos 3\theta_{ij}) \qquad \text{ii}$$

and trigonal carbon, respectively. The ethane potential barrier V_0 = 2.800 kcal./mole and a bond-bending force constant[12] of $k/2$ = 0.0175 kcal./mole were employed to give the strain energies of the maximally puckered models. Thus the total energy required to deform the interior angles of the ring in the envelope form is

$$\begin{aligned} V_B &= 0.0175\,(3(109.5 - \omega_1)^2 + 2(109.5 - \omega_3)^2) \\ &= 3(2.912) + 2(0.473) = 9.68 \text{ kcal./mole} \end{aligned}$$

as there are three angles with the magnitude of ω_1 and two with that of ω_3. And, the total torsional strain energy of the half-chair is

$$\begin{aligned} V_t &= 1.400\,(2(1 + \cos 3 \times 19.0) + 2(1 + \cos 3 \times 50.0) \\ &\qquad + (1 + \cos 3 \times 60.0)) \\ &= 1.400\,(2 \times 1.545 + 2 \times 0.134 + 0.000) \\ &= 4.326 + 0.376 = 4.70 \text{ kcal./mole} \end{aligned}$$

as there are two angles of 19.0°, two of 50.0° and one of 60.0° in this model.

However the above considerations are not enough. It is necessary to include the electron correlation energies (London or dispersion energies) in accord with Pitzer's significant discovery[4] that inclusion of this energy leads ultimately to reasonably good heats of formation of cyclic hydrocarbons. The zero point vibrational energy and heat of bond formation given by Pitzer and Donath in their work are retained.

While the data in Table II will be utilized in detail in a companion paper and later reports, it does help to illuminate a question we had wondered about earlier. We had found that cyclopentane and cyclohexane compounds behaved similarly toward four-center type reactions.[3] These reactions are of the type where maximum speed is obtained by coplanarity of the four centers of importance. Table II helps explain why the two rings might behave similarly. A simple monosubstituted ring such as cyclopentyl chloride would according to our present estimates be puckered about as much as cyclopentane itself. If the ring is in the envelope conformation and at least some of the chloride is axial, then *trans*-hydrogens will not be quite coplanar with the chlorine for easy E_2 elimination. However, the cost of puckering the ring a bit further if this is required such that the *trans* diaxial groups are now coplanar is about 9.02–7.35 = 1.67 kcal. The range for the half-chair is 8.49 − 7.64 = 0.85 kcal. It is therefore apparent that the range of energy differences is sufficiently small so that the cyclopentane ring can compete successfully with the cyclohexane ring toward four-center reactions.

At the equilibrium position for cyclopentane itself, Pitzer and Donath found that the envelope was slightly more stable than the half-chair by 0.53 kcal.[4] We find in the maximally puckered models in Table II that the electron correlation value for the envelope is again less than for the half-chair, but the effect is partially wiped out in the

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[11] P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 182 (1961), and references quoted therein.

[12] The available information on force constants for deforming certain C–C–C angles is disappointingly limited. For example, the force constant for deforming the 116.3° C–C–C angle of acetone or other simple ketones is unknown and must be estimated. For a scholarly discussion of force constants and related material see Westheimer's chapter in M. S. Newman, "Steric Effects in Organic Chemistry," J. Wiley and Sons, Inc., New York, N. Y., 1956, Chapt. 1.

envelope by the rapid increase of bond bending strain so that the two heats of formation, 7.35 *vs.* 7.64 kcal., are nearly equal.

It is important to note that the treatment above does not include calculations of repulsive van der Waals forces. They are not operative in these simple models since the closest approach of 2,5-diaxial protons in the envelope is 2.22 Å., a separation which is greater of 2,5-diaxial protons in the envelope is 2.22 Å., a separation which is greater than their collision diameter.

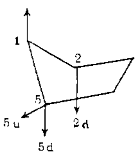
On substitution it will often prove the case that some internuclear distances will give rise to considerable van der Waal's repulsion. In order that these repulsions can be estimated, the coördinates of the ring atoms and unit vectors for substituents are given in Table III.

TABLE III

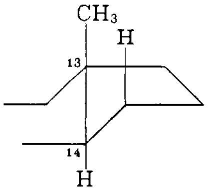
Envelope model (VI)				Half-chair model (III)			
Coördinates of the carbon nuclei coördinate				Coördinates of the carbon nuclei coördinate			
Atom	x	y	z	Atom	x	y	z
1	0.000	0.000	0.400	1	0.000	0.000	0.000
2	0.725	1.150	−.324	2	0.959	1.183	−.229
3	2.148	0.770	.124	3	2.283	0.675	.370
4	2.148	−0.770	.124	4	2.283	−0.675	−.370
5	0.725	−1.150	−.324	5	0.959	−1.183	.229
Unit vectors for tetrahedral substituents				Unit vectors for tetrahedral substituents			
1u[a]	.169	0.000	.986	1u	−0.576	0.155	0.802
1d[b]	−.986	.000	−.168	1d	−.576	−.155	−.802
2u	−.280	.900	.332	2u	−.319	.822	.476
2d	−.114	−.039	−.992	2d	.099	.202	−.975
3u	.190	.354	.915	3u	−.050	−.103	.994
3d	.679	.354	−.642	3d	.780	.575	−.244
4u	.190	−.354	.915	4u	.780	−.575	.244
4d	.679	−.354	−.642	4d	−.050	.103	−.994
5u	−.280	−.900	.332	5u	.099	−.202	.975
5d	−.114	.039	−.992	5d	−.319	−.882	−.476
Unit vectors for trigonal bonding				Unit vectors for trigonal bonding			
1t[c]	−0.708	0.000	0.707	1t	−1.000	0.000	0.000
2t	−.341	.746	−.572	2t	−0.191	.887	−.432
3t	.753	.614	.237	3t	.642	.409	.649
4t	.753	−.614	.237	4t	.642	−.409	−.649
5t	−.341	−.746	−.572	5t	−.191	−.887	.432

[a] Where u means up. [b] Where d means down. [c] Where t means trigonal.

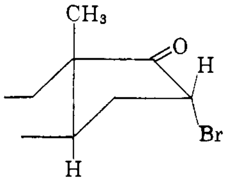
Internuclear Distances.—The beginning of the unit vector 5d (*V*) is located at C_5's, x, y, z coördinates. How does one obtain the coördinates of 5d's terminus? This is done by using C_5's x, y, z coördinates and adding or subtracting the corresponding x, y, z values for 5d given in Table III. This has the effect of a movement from C_5 along 5d to its terminus.



V



VI



VII

The reason for doing it this way is that the x, y, z values in Table III for 1u, 1d, 2u, etc., are set up to be a measure of the distance of each terminus from the parent carbon atom based on a unit vector (unit movement). Therefore if 5d were assumed to be an axial carbon atom attached to C_5 it would be longer (1.54 Å.) than unity, hence each x, y, z value for 5d in Table III must be multiplied by 1.54 before addition or subtraction to C_5's x, y, z coördinates. These new coördinates, x (0.549), y (−1.090) and z (−1.852) are now those of an axial carbon atom on C_5 such as might be the case for an axial methyl group. It might be pointed out that in the example below, i. j and k are unit vectors along the x, y, z axes, respectively

$$\begin{aligned} 1.54 \times 5\text{d} &= 1.54\,(-0.114i - 0.039j - 0.992k) \\ &= -0.176i - 0.060j - 1.528k \\ C_5 &= \underline{0.725i - 1.150j - 0.324k} \\ \text{Axial C atom} &= 0.549i - 1.090j - 1.852k \end{aligned}$$

Similarly for the 2d proton on C_2 its coördinates (for C–H equal to 1.10 Å.) turn out to be $0.600i + 1.107j - 1.415k$. Now to obtain the internuclear distance between the CH_3 and C_2 proton one takes the square root of the sum of the squares of the differences in like coördinates which in this case turns out to be 2.24 Å.

$$CH_3,\ \text{H distance} = 2.24 = [(0.600 - 0.549)^2 + (1.107 + 1.090)^2 + (-1.415 + 1.852)^2]^{1/2}$$

This is well within the sum of the van der Waals radii of these two groups and corresponds to considerable repulsive energy. Since structure V above is analogous upon rotation to VI, a possible conformation of a steroid ring D, we have, in principle, by the method outlined above analyzed the C_{13} methyl–C_{15} hydrogen interaction in a C/D *trans* fused steroid.

Dipole Moments.—The unit vectors of Table III also present a convenient method of calculating the dipole moments of cyclopentane systems. Thus we may wish to consider the dipole moments of the 16α-bromo-17-ketosteroids which have been assigned the envelope conformation (VII) on the basis of spectral data.[1,13] Bond moments for the carbonyl group and the carbon–bromine bond are taken as 2.91 and 2.10 D., respectively, in accord with the observed moments of the chloro- and bromocamphors.[3,14] Here the appropriate unit vectors are treated as having unit dipole moment; hence each must be multiplied by the appropriate total moment for each group.

Further the U_{C-O} involves a trigonal carbon atom; hence $4t$ of the envelope must be used for this group. Using the unit vector $3u$ for C—Br and $4t$ for C=O there is obtained

$$u_{C-Br} = 2.10\ (0.190i + 0.354j + 0.915k) = 0.399i + 0.743j + 1.922k$$

$$u_{C-O} = 2.91\ (0.753i - 0.614j + 0.237k) = 2.191i - 1.787j + 0.690k$$

The vector sum of the bond moments, $u_{C-Br} + u_{C=O} = u_{\text{total}}$, gives the coördinates of the molecules total moment, $u_{\text{total}} = 2.590i - 1.044j + 2.612k$. Then $u^2 = (2.5901)^2 + (-1.044)^2 +$

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(13) J. Fishman and C. Djerassi, *Experientia*, **15**, 138 (1960); J. Fishman, *J. Am. Chem. Soc.*, **82**, 6143 (1960).

(14) W. D. Kumler, N. Pearson and F. V. Brutcher, Jr., *ibid.*, **83**, 2711 (1961).

$(2.612)^2$ gives the magnitude of the moment (3.82 D.). This value is in excellent agreement with the observed moment of 16α-bromo-5α-androstan-17-one which we have measured in benzene solution at 25° and found to be 3.85 D.[15]

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[15] Unpublished data of F. V. Brutcher, Jr., and F. J. Reynolds.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA, PHILADELPHIA 4, PENNA.]

The Conformations of Substituted Cyclopentanes. III. Ring D in the Steroids[1,2]

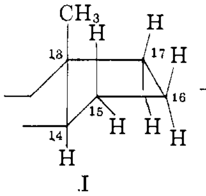
BY FREDERICK V. BRUTCHER, JR., AND WILLIAM BAUER, JR.

RECEIVED AUGUST 30, 1961

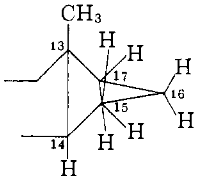
The previously-described,[1] maximally-puckered models for the symmetrical forms of cyclopentane have been applied to the description of three possible conformations of ring D in the steroids. Calculation of bond-bending and torsional energies as well as interaction energies for 1,3-substituents has suggested general stability relationships for these conformations on substitution of the ring. Infrared data on steroid haloketones and glycols have been utilized in assignment of conformation to several steroids. Some of the chemistry of ring D is discussed in the light of the conformations of the ring.

The most famous relative of the simple cyclopentane ring is certainly the five-membered ring D of the steroids.[3-7] In a previous paper we have constructed by vector analytical techniques[1,8] models of maximally puckered cyclopentane rings such as would be found in the *trans*-locked C/D ring system. In this paper we apply these models to ring D and interpret some of its chemistry.

As a first step, the three symmetrical conformations of ring D were constructed (I, II, III). Conformations I and II have been previously recorded in the literature while III has been hitherto neglected. Envelope conformation I[2] is that which has earlier been generally used by chemists having had its birth in Barton's original drawing of the steroid molecule.[9] Envelope I has C_{14} below the plane of C_{13}, C_{15}, C_{16}, C_{17}. Half-chair II is an arrangement which has been discussed in detail for simple cyclopentanes[2]; it has C_{13} above and C_{14} an equal distance below the C_{15}, C_{16}, C_{17} plane. Finally there is the previously neglected envelope III. This last conformation has C_{14}, C_{15}, C_{16} and C_{17} in a single plane while C_{13} lies above the plane.[10]



I



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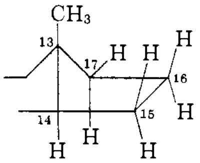

III

The next step in our analysis was to compare these three conformations with regard to their torsional (V_t) and angle-strain (V_B) energies, their electron-correlation energies (E_c) (London or dispersion energies) and any significant 1,3-interactions of a repulsive nature (van der Waals repulsive forces). In view of the laborious mathematical operation of summing up all C–C, C–H and H–H non-bonded London interactions, it was convenient to assume that the London force difference between envelope I (or III) and half-chair II is essentially the same as in the parent, unsubstituted, maximally-puckered models. Here[1] the envelope (E_c −47.95 kcal./mole) is stabilized 0.66 kcal./mole more than the half-chair (E_c −47.29 kcal./mole) or, in other words, the half-chair has 0.66 kcal./mole more energy than the envelope due to the London force effect. We therefore add 0.66 kcal./mole to the half-chair II when bond-bonding and torsional energies are being calculated.

For cases where interior angle strain energy and also correlation energy can be taken to be the same as in the parent conformations a new correction factor of 0.33 kcal./mole is of use. Substitutions of the type such as methyl, halogen or hydroxyl which change only the torsional energy would lead to this situation. This correction factor is derived by noting that the difference in bond-bending energies between the envelope (9.68 kcal./mole) and the half-chair (8.69 kcal./mole) favors the half-chair by 0.99 kcal./mole When this quantity is combined with the correlation energy difference (−0.66 kcal./mole) one arrives at the factor 0.33 kcal./mole favoring the half-chair; this energy is then added to envelope conformations I and III.

Another important factor does exist. In addition to the above energy terms the axial methyl group on C_{13} has the potentiality of strong interaction of repulsive, van der Waals type with the hydrogens at C_{15} and C_{16}. The earlier calculations for our unsubstituted models did not require in-

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[1] Paper II, F. V. Brutcher, Jr., and W. Bauer, Jr., *J. Am. Chem. Soc.*, **82**, 2233 (1962); see also F. V. Brutcher, Jr., and W. Bauer, Jr., *Science*, **132**, 1489 (1960).

[2] F. V. Brutcher, Jr., T. Roberts, S. J. Barr and N. Pearson, *J. Am. Chem. Soc.*, **81**, 4915 (1959).

[3] See L. F. Fieser and M. Fieser, "Steroids," Reinhold Publishing Corp., New York, N. Y., 1959.

[4] Eliel and Pillar[5] as well as Dauben and Pitzer[6] have considered the distortion in a cyclohexane ring arising upon fusion to a cyclopentane ring. They conclude that in the *trans* isomer the distortion is toward a more severe chair conformation. In hydrindane this causes crowding of the axial hydrogen atoms. When one of these is replaced by a methyl group as in the steroids, distortion of the cyclohexane ring in this fashion is, hence, exceedingly costly energywise and one expects it to be at a minimum. Eliel has presented experimental data which verify the existence of these distortions and at the same time indicate that they are, indeed, small.[5] With regard to the five-membered ring in the hydrindanes, Allinger and Coke (*J. Am. Chem. Soc.*, **82**, 2553 (1960)) have found that the *cis* isomer has a larger entropy and point out that this may be due to a larger partial pseudorotation (*cf.* J. P. McCullough, *J. Chem. Phys.*, **29**, 966 (1958)) in the *cis* isomer.

[5] E. L. Eliel and C. Pillar, *J. Am. Chem. Soc.*, **77**, 3600 (1955).

[6] W. G. Dauben and K. S. Pitzer in M. S. Newman, "Steric Effects in Organic Chemistry," J. Wiley and Sons, Inc., New York, N. Y., 1956, p. 37.

[7] For a discussion of several steroidal hydrindanones, see Fieser and Fieser, ref. 3, page 211 ff.

[8] K. S. Pitzer and W. N. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959).

[9] D. H. R. Barton, *J. Chem. Soc.*, 1027 (1953).

[10] These three conformations may be considered to arise through a partial pseudorotation, the ring fusion preventing the full pseudorotation cycle from taking place.