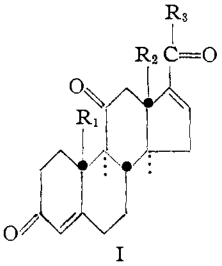
tive which was condensed with 4-diethylamino-2-butanone methiodide in the presence of potassium *t*-butoxide to produce 1,9,10,10a-tetrahydro-7-methoxy-3(2H)-phenanthrone III, R_2 = CH_3, R_3 = H (m.p. 87–87.5°), λ_{max}^{EtOH} 328 mμ, ϵ 22,000. Found: C, 79.35; H, 7.38). Reduction of III with sodium borohydride gave the corresponding alcohol (m.p. 105–106°. Found: C, 78.61; H, 8.15) which was reduced catalytically over palladium on strontium carbonate to a single saturated alcohol (m.p. 117–119°. Found: C, 77.97; H, 8.92). Reduction of the anisole ring with lithium and liquid ammonia, followed by cleavage of the resulting enol ether with concentrated hydrochloric acid, yielded the α,β-unsaturated ketone IV as a single isomer (m.p. 137–138°. Found: C, 77.17; H, 9.48. Semicarbazone, m.p. 231–233°, dec. Found: C, 66.00; H, 8.57). 3-Benzyloxybutyl iodide was synthesized by addition of benzyl alcohol to ethyl crotonate, followed by reduction to 3-benzyloxy-1-butanol (b.p. 98–107° (1 mm.); Found: C, 73.29; H, 8.72) which was transformed with phosphorus tribromide into the corresponding bromide (b.p. 83–86° (0.5 mm.); Found: C, 54.36; H, 6.47; Br, 32.77). The benzoate of IV (m.p. 143–144°; Found: C, 77.96; H, 7.62) was transformed into its potassium enolate by removal of the *t*-butyl alcohol from its solution in benzene containing one equivalent of potassium *t*-butoxide. This was alkylated with 3-benzyloxybutyl bromide or iodide to give mainly monoalkylated product[6] V which was alkylated again with methyl iodide by the same procedure. Transformation to tetracyclic ketones VIIA and VIIB was carried out, without isolation of intermediates, by ketalization with ethylene glycol-*p*-toluenesulfonic acid, removal of the benzyl group with sodium in liquid ammonia, oxidation with chromic acid-pyridine, acid-hydrolysis of the cyclic ketal and, finally, base cyclization. Fractional crystallization of the tetracyclic ketone mixture from ethyl acetate–cyclohexane gave roughly equal amounts of VIIA (m.p. 206°; Found: C, 80.65; H, 8.90) and its C_{10} epimer, VIIB (m.p. 148°; Found: C, 80.51; H, 8.57).

Reduction of VIIA with sodium borohydride in ethanol and reoxidation with manganese dioxide in chloroform gave $\Delta^{4,9(11)}$-D-homoandrostadien-16-ol-3-one (m.p. 186–188°; Found: C, 79.96; H, 9.59). Transformation into the tosylate (m.p. 173–174°, dec.), followed by refluxing with collidine gave $\Delta^{4,9(11),16}$-D-homoandrostatrien-3-one, m.p. 150.8–151.8°, identical with a sample kindly supplied by Dr. W. S. Knowles.[2b] The stereochemistry of VIIA is thus confirmed. Introduction of an 11-keto group was easily accomplished by conversion to the 9,11-bromohydrin, oxidation to the 9-bromo-11-keto compound and reduction with chromous chloride[7] to the desired Δ^4-3,11,16-D-homoandrostenetrione, II (R_1 = R_2 = CH_3, R_3 = H; m.p. 206.5–208°. Found: C, 76.72; H, 8.54).

Alternatively, IV as its acetate (m.p. 137–138°; Found: C, 73.86; H, 8.89) was ozonized in ethyl acetate and the enol lactone of the resulting keto acid was treated at −30° in ether with the grignard reagent from 5-chloro-2-methyl-1-pentene[8] (b.p. 127–129.5°. Found: C, 60.85; H, 9.72; Cl, 29.60). Cyclization of the resulting product with base yielded VI, isolated as its *p*-bromobenzoate (m.p. 105–107.5°; 129°. Found: C, 66.83; H, 6.87; Br, 16.26). The latter was alkylated with methyl iodide as in the benzyloxybutyl series, and the resulting C_{10} epimers were separated as *p*-nitrobenzoates yielding *p*-nitrobenzoate A (m.p. 157–158°. Found: C, 72.28; H, 7.79; N, 2.88) and *p*-nitrobenzoate B (m.p. 148°. Found: C, 72.21; H, 7.70; N, 2.94). The *p*-nitrobenzoate A was the predominant isomer (2:1) and its stereochemistry at C_{10} was the desired one since on ozonolysis, followed by base cyclization, it produced the same $\Delta^{4,9(11)}$-D-homoandrostadien-16-ol-3-one that has been described above.

Experiments are in progress with III, R_2 = R_3 = CH_3; and R_2 = CO_2R, R_3 = CH_3.



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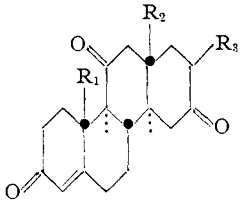

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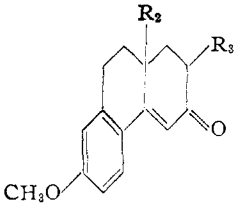

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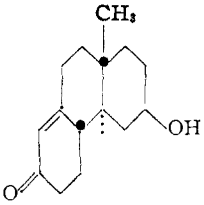

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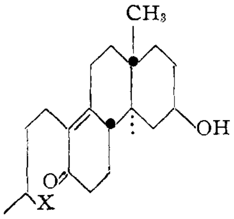
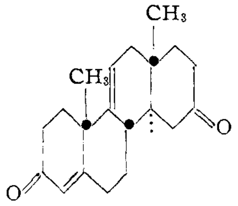


V, X = $C_6H_5CH_2O$—
VI, X = CH_2=



VIIA

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[6] For related monoalkylations of enones, see J. M. Conia, *Bull. soc. chim.*, 690, 943 (1954).

[7] *Cf.* J. Fried and E. F. Sabo, THIS JOURNAL, **75**, 2273 (1953).

[8] Synthesized by boron fluoride-etherate catalyzed addition of ketene to 5-chloro-2-petanone and thermal decomposition of the resulting β-lactone.

CHANDLER LABORATORY GILBERT STORK
COLUMBIA UNIVERSITY H. J. E. LOEWENTHAL
NEW YORK 27, NEW YORK P. C. MUKHARJI

RECEIVED JANUARY 3, 1956

THE CRYSTAL STRUCTURE OF AMMONIA-BORANE, H_3NBH_3

Sir:

Recently Shore and Parry[1] described a new compound, H_3NBH_3, and as evidence of crystallinity they outlined its X-ray diffraction powder pattern.

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[1] S. G. Shore and R. W. Parry, THIS JOURNAL, **77**, 6084 (1955).

From these data it has proved possible to determine its crystal structure.

The table displays the spacings, d_0, and intensities, I_0, given by Shore and Parry in comparison with those calculated from the proposed structure, d_c and I_c. The indices *hkl* relate to a tetragonal cell with a = 5.255 Å. and c = 5.048 Å., derived from a least squares fitting of the cell to the data after indices had been derived by trial-and-error. The indices indicate body-centering. With two molecules per cell the calculated density is 0.740 g./cm.^{3}, a reasonable value when compared with the density of solid ethane.

TABLE I

hkl	d_0, Å.	d_c, Å.	I_0	I_c
110	3.72	3.716	VVS	12,200
101	3.65	3.641	VS	10,100
200	2.63	2.628	S	2,930
002	2.52	2.524	MS	473
211	2.13	2.131	S	2,150
112	2.09	2.088	MS	758
220	1.86	1.858	W	548
202	1.82	1.820	W	341
310	1.66	1.662	MW	594
301	...	1.655	...	248
103	1.60	1.603	MS	782
222	...	1.496	...	85
321	1.40	1.400	VW	163
312	...	1.388	...	104
213	1.37	1.368	W	554
400	...	1.314	...	63

With two molecules in a body-centered cell, the molecule is the asymmetric unit and must lie on the four-fold axis and the molecule must either rotate about the axis or orient at random with regard to rotation about it in order to conform statistically to the four-fold symmetry. The structure is built up from one such molecule by the translations of the body-centered tetragonal lattice. The space group is I4mm. Another structure with more disorder with the B–N bonds pointing up and down the c axis at random has the space group I4/mmm. It appears improbable because the molecule is expected to have a considerable dipole moment, which would favor the polar arrangement. Moreover, the intensities, although similar, are slightly different and calculations favor the polar form.

The nitrogen atom is at 0,0,0 and the boron at 0,0,z with z selected to give the best agreement between calculated and observed intensities. Special consideration was given to those reflections not observed although permitted by the cell. The scattering factors are those of McWeeny[2] with the scattering power of two hydrogens added to each to allow roughly for the hydrogens of the molecule. The multiplicity, Lorentz and polarization factors are included, assuming that Cu Kα rays were used by Shore and Parry. An asymmetric temperature factor of the form $\exp[-\alpha(h^2 + k^2) - \beta l^2]$ was used, with $\alpha = 0.08$ and $\beta = 0.03$, for direct application to intensities.

The agreement is as good as the qualitative nature of the data will permit. The parameter z is 0.31 ± 0.01, and the B–N distance is 1.56 ± 0.05Å. Each boron has as nearest neighbors on other molecules one nitrogen at 3.49 Å. along the c axis and four nitrogens at 3.84 Å. on molecules produced by the body-centering. Each nitrogen has a similar set of borons as nearest neighbors. As one expects the borons and nitrogens to carry opposite formal charges, this arrangement leads to charge compensation between neighbors.

CONTRIBUTION NO. 2063
GATES AND CRELLIN LABORATORIES EDWARD W. HUGHES
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

RECEIVED DECEMBER 16, 1955

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[2] R. McWeeny, *Acta Cryst.*, **4**, 513 (1951).

THE STRUCTURE OF H_3NBH_3

Sir:

The preparation, chemical properties and approximate molecular weight of H_3NBH_3 have been determined by Shore and Parry,[1] who also indicated its crystalline nature. We have determined the crystal structure from a sample supplied to us by Professor R. W. Parry, and have strong supporting evidence that the monomeric formula H_3NBH_3 is correct.

Powder diffraction patterns, taken both on film in a cylindrical camera and on the General Electric XRD-3 unit, were readily indexed on a tetragonal unit cell with dimensions a = 5.234 and c = 5.027 Å. (λ = 1.542 Å.). Observation of reflections only when $h + k + l$ is even indicated a body centered unit cell, thus requiring an even number of molecules. An experimental observation that the density of the material is less than that of water then indicated only two molecules in the unit cell and thus led to a calculated density of 0.74 g. cm.$^{-3}$. Normal decline of the *hk*0 intensities, and a positive pyroelectric test then led to a structure in the polar space group C_{4v}^9—I4mm., in which all B–N bonds have the same orientation along the c axis. Consequently, the atomic positions are $0,0,z_B$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z_B$; $0,0,z_N$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2} + z_N$. The only short B–N distance, obtained from $z_B - z_N = 0.32$, is 1.6 Å. Hydrogen atoms were not located, but were introduced into the calculated structure factors (Table I) as axial rotators about the B–N axis, since orientational disorder or rotation is indicated by the four-fold axis along the B–N axis.

The crystal structure is very similar to that[2] of HCN, and certain aspects of that determination apply here. For example, the thermal motion is anisotropic, thus requiring the temperature factor $\exp[-0.023(h^2 + k^2) - 0.013l^2]$, which has been multiplied into the $F_{\text{calcd.}}$ (Table I). Also a transition has been observed at −43 ± 5° which leaves the major features of the structure unchanged, and causes the appearance of only very faint additional lines in the powder pattern. As in the HCN, there is a strong interaction of the scale and temperature factors with the distance parameter which causes the probable error of the B–N distance to be very large, about 0.2 Å. Finally, the non-polar structure based on the space group D_{2h}^7—$P_{4/n}$ mm was

---

[1] S. G. Shore and R. W. Parry, THIS JOURNAL, **77**, 6084 (1955).

[2] W. J. Dulmage and W. N. Lipscomb, *Acta Cryst.*, **4**, 330 (1951).