structure of boron appears to be very difficult but not insoluble. Further progress with the detailed investigation has been made and the work will be continued in this Laboratory.

Acknowledgment.—The authors wish to thank Professor C. C. Murdock for his assistance in the X-ray investigations, Professor C. W. Mason and Dr. W. C. McCrone, who aided in the optical examinations, Dr. G. R. Finlay and J. A. Robertson who helped with the analytical work, and the Norton Company of Chippawa, Ontario, Canada, for supplying the sample of boron carbide.

The crystalline boron made available by this work is being used for the investigation of the thermochemistry of this element and the characteristics of the powdered and vitreous forms are being studied.

Summary

1. The factors affecting the preparation of boron by the filament method and the types of products obtained have been studied.
2. Single crystals of boron of high purity and appreciable size have been grown.
3. Large single crystals were found in the form of needles or hexagonal plates. Smaller crystals were observed as hexagonal rods or massive in form. Optical evidence indicates that both the needle and plate forms of crystalline boron may belong to the monoclinic system.
4. Crystalline boron shows great resistance to attack by various chemical reagents including oxygen and oxidizing agents. This is in contrast to the great reactivity shown by the element in finely divided form.
5. Crystalline boron shows the extreme hardness, great opacity, metallic luster, and electrical properties usually associated with semi-metallic solids.
6. Measurements of the temperature coefficient of electrical resistance indicate that this effect is much smaller than has been previously reported; between 20 and 600° the increase in conductivity observed is less than one hundred fold.
7. An X-ray powder diffraction pattern suitable for the identification of crystalline boron has been established.
8. Analysis of X-ray diffraction patterns of the needle crystals indicates a spacing of 5.06 Å. along the needle axis, with two equal and orthogonal axes 8.93 Å. in length lying in a plane perpendicular to the needle axis. The needle crystals were invariably found to be interpenetration twins, the components twinning along (130) with the needle axis in common. The unusual amount of symmetry shown by the needle crystals indicates that the natural system of this form of crystalline boron may be tetragonal under ideal conditions of crystal growth.
9. The smallest cell based on orthogonal axes found for the plate crystals has a = 17.86, b = 8.93, c = 10.13 Å. No case of twinning was observed for these crystals. It seems probable that the structures of the two crystalline forms are not fundamentally different but the doubling of two of the corresponding translations in the needles cannot be explained in detail at this time.

ITHACA, N. Y. RECEIVED JUNE 14, 1943

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Hyperconjugation in Methyl Butadienes as Shown by Dipole Moments

BY N. BRUCE HANNAY AND CHARLES P. SMYTH

Dipole moment measurements have given significant evidence as to hyperconjugation in the molecules of aldehydes, nitriles and chlorides, in which the presence of strongly electronegative atoms markedly increases the extent of the hyperconjugation.[1] The dipole moments found for a number of unsaturated hydrocarbons gave sufficient evidence of hyperconjugation in their molecules to warrant the use of moment measurements in the investigation of the simple substituted butadienes.

The dielectric constants of the vapors were measured with the apparatus and technique previously described.[2-5] The measurements on 2,3-dimethylbutadiene were made by the "extrapolation method," in which the effects of devia-

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[1] Hurdis and Smyth, THIS JOURNAL, **65**, 89 (1943).

[2] McAlpine and Smyth, *ibid.*, **55**, 453 (1933).

[3] deBruyne and Smyth, *ibid.*, **57**, 1203 (1935).

[4] Wiswall and Smyth, *J. Chem. Phys.*, **9**, 352 (1941).

[5] Hurdis and Smyth, THIS JOURNAL, **64**, 2829 (1942).

tions from the gas laws were eliminated by measurement over a wide range of pressure, and, on the other substances, by the "two-point" method, in which the dielectric constant was measured at two pressures only. The absolute accuracy of the method has been shown by previously published checks[5] of values established by other work. It is close to the relative accuracy evident in the data in Table I.

Materials

Butadiene, probably containing no more than 1% of impurity, was procured in a cylinder from the Ohio Chemical Company. It was run directly into the apparatus and measured without purification. The other substances were given us by the Standard Oil Development Company, to whom the authors wish to express their gratitude. Each liquid was distilled from a trap attached to the dielectric constant apparatus into a manometer tube, from which it was caused to vaporize into the dielectric cell for measurement. These two distillations should have effectively removed from each sample the trace of inhibitor, which had, in each case, a relatively high boiling point.

Experimental Results

The results of individual runs are given in Table I for the polarization, P, for all the substances. Where the use of the two-point method of measurement increased the error in individual P values, several runs were made at each temperature and the average of the P values, P_{av}, was used instead of a single value to calculate the moment, μ, listed in the last column. The molar refraction for the sodium D line, MR_D, used in calculating the moment is listed in Table II, together with the average of the moment values for each substance.

The refractions were taken from Landolt–Börnstein or calculated from the atomic refractions and the probable exaltations[6] with slight adjustments of the calculated values to make them consistent with the observed. The possible errors in these values used in calculating the moment as $\mu = 1.28 \times 10^{-20} [(P - MR_D)T]^{1/2}$ are less important than the uncertainties arising from ignorance of the small atomic polarizations. The uncertainty is serious only in the case of butadiene where the difference between the total polarization and the induced polarization may be zero, giving zero moment, or as large as 1, giving a moment 0.27. The slight apparent decrease in polarization with rising temperature also corresponds to a moment of about 0.27, but the temperature dependence of the polarization is so small as to lie within the possible experimental error as evidenced by the variations among the polarization values at one temperature. Many investigators add 5% of its value to the molar refraction to obtain the induced polarization. If this were done for butadiene, the lowest possible value of the refraction would yield a zero moment value. It may, therefore, be concluded that the moment of butadiene is indistinguishable from zero in these measurements and certainly not far

TABLE I

POLARIZATIONS AND DIPOLE MOMENTS

T, °K.	P		P_{Av}	$\mu \times 10^{18}$
Butadiene				
299.4	21.58	22.08	21.98	0
	22.25			
339.1	21.62	21.88	21.77	0
	21.88	21.69		
380.2	21.52	21.96	21.76	0
	21.71			
443.1	21.70	21.71	21.62	0
	21.54	21.54		
461.6	21.70		21.70	0
1-Methylbutadiene				
388.9	33.06	32.55	32.43	0.68
	32.03	32.11		
	32.40			
425.7	32.23	32.15	31.81	.68
	31.34	31.51		
468.7	31.71	30.69	31.01	.67
	30.62			
2-Methylbutadiene				
358.1	27.85	27.99	27.93	.40
	27.94			
381.9	27.49	27.70	27.47	.38
	27.13	27.20		
	27.85			
413.8	27.13	27.23	27.18	.37
418.3	27.13	27.17	27.15	.37
445.2	27.29	27.18	27.26	.38
	27.45	27.11		
476.7	26.75	27.24	27.03	.38
	27.02	27.10		
2,3-Dimethylbutadiene				
371.3	34.17			.52
388.0	34.04			.52
409.2	33.77			.52
452.9	33.40			.52
483.8	33.04	32.84		.51

TABLE II

MOLAR REFRACTIONS AND MOMENT VALUES

	MR_D	$\mu \times 10^{18}$
Butadiene	21.6 (calcd.)	(0)
1-Methylbutadiene (*trans*)	25.3	0.68
2-Methylbutadiene	25.22	.38
2.3-Dimethylbutadiene	29.75	.52

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(6) Auwers and Eisenlohr, *J. prakt. Chem.*, **84**, 1 (1911).

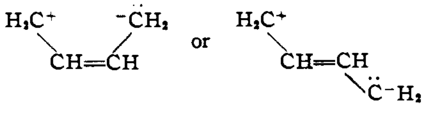
from zero. The uncertainties in the larger moments of the other three compounds are much less, being less than 0.1 for 2-methylbutadiene, 0.07 for 2,3-dimethylbutadiene and 0.05 for 1-methylbutadiene.

Discussion of Results

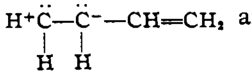
The zero or extremely small moment value found for butadiene does not throw much light upon the question as to its existence in a *cis* form or a *trans* form with respect to the central C–C bond or a mixture of the two with the *trans* predominating. The *trans* form should have zero moment while the *cis* form should have a small moment, which, however, might easily be too small for detection even if the *cis* form made up a considerable fraction of a mixture of *cis* and *trans* forms. The more probable resonating forms may be written

$$\mathrm{H_2C{=}CH{-}CH{=}CH_2,\ H_2C^+{-}CH{=}CH{-}\ddot{C}H_2^-,\ H_2\ddot{C}^-{-}CH{=}CH{-}C^+H_2}$$

The polarity arising from one polar structure just cancels that from the other, no matter whether the molecular form is *cis* or *trans* with respect to the central bond.

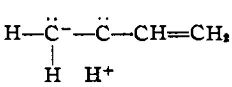


However, four structures such as



$$\mathrm{H^+}\underset{\mathrm{H}}{\ddot{\mathrm{C}}}\mathrm{-}\underset{\mathrm{H}}{\ddot{\mathrm{C}}}\mathrm{^-{-}CH{=}CH_2}$$

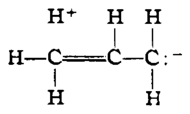
and two structures such as



$$\mathrm{H{-}}\underset{\mathrm{H}}{\ddot{\mathrm{C}}}\mathrm{^-{-}}\underset{\mathrm{H^+}}{\ddot{\mathrm{C}}}\mathrm{{-}CH{=}CH_2}$$

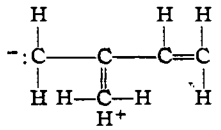
may be written. The contributions of the four structures should overbalance those of the two and give rise to a small dipole in each half of the molecule. In the *trans* form these two dipoles should oppose and cancel each other, but, in the *cis* form, they should cause the molecule to have a small moment, perhaps, too small to detect.

Analogous polar structures for the symmetrical ethylene molecule cancel one another's polarities leaving the moment zero, but, in the case of the propylene molecule, as previously pointed out,[1] structures such as



$$\begin{array}{ccccc} & \mathrm{H^+} & \mathrm{H} & \mathrm{H} & \\ \mathrm{H}- & \mathrm{C} & = & \mathrm{C}-\mathrm{C} & :^- \\ & \mathrm{H} & & \mathrm{H} & \end{array}$$

give rise to a moment, 0.35. Analogous structures for isoprene, or 2-methylbutadiene

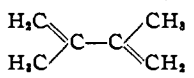


$$\begin{array}{cccccc} & \mathrm{H} & & & \mathrm{H} & \mathrm{H} \\ ^-: & \mathrm{C} & - & \mathrm{C} & - & \mathrm{C}{=}\mathrm{C} \\ & \mathrm{H} & & \mathrm{H{-}\overset{\|}{C}{-}H} & & \mathrm{H} \\ & & & \mathrm{H^+} & & \end{array}$$

should give rise to a similar moment.

The amount of the contribution of structures of this type should be somewhat less than that in the case of propylene as the amount of double bond character of the central butadiene bond should reduce that of the bond to the methyl carbon. Although the observed moment value, 0.38, for 2-methylbutadiene in Table II may be somewhat high, the fact that it is indistinguishable from that of propylene indicates that the polarities of the other possible types of contributing polar structures approximately cancel one another. This would occur if the molecule were *trans* in form or if the hyperconjugated structures with H⁺ such as those written for butadiene make such small contributions as to cause a negligibly small moment in the *cis* form. This reasoning strengthens the conclusion that the unsubstituted butadiene molecule has a moment indistinguishable from zero, a conclusion consistent with the indications of electron diffraction that "butadiene molecules must be essentially coplanar and *trans*"[7] and with the conclusion of Mulliken[8] that the *trans* arrangement is the actual or, at least, the predominant form in butadiene. The moment of 2-methylbutadiene does not appear to give evidence as to the shape of the molecule, but gives support to the theory of hyperconjugation in such compounds.

The *trans* form of 2,3-dimethylbutadiene



should obviously have zero moment, while consideration of the interatomic distances and valence angles leads to the conclusion that in the *cis* form, the dipoles in the two halves of the molecule, each approximately equal to that in the 2-methylbutadiene molecule, should point nearly in the same direction and give a resultant moment approximately twice that of 2-methylbutadiene. The moment value, 0.52, for 2,3-dimethylbutadiene in Table II is less than twice that of 2-methylbutadiene but is so large as to

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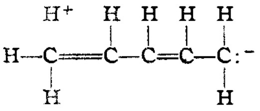
[7] Schomaker and Pauling, THIS JOURNAL, 61, 1769 (1939).

[8] Mulliken, *Rev. Modern Phys.*, 14, 265 (1942).

show that the *cis* structure must predominate largely over the *trans*. If the 2-methylbutadiene moment value 0.38 is high by as much as 0.10, which is not impossible, the observed 2,3-dimethylbutadiene moment would agree within its experimental error with the value calculated for the *cis* form. This establishment of the large predominance of the *cis* form agrees with the conclusions of Mulliken[8] that spectroscopic results look almost as if 2,3-dimethylbutadiene were pure *cis*.

In 1-methylbutadiene, *trans*-piperylene, polarity should arise from polar structures analogous to those which have been proposed for propylene and 2-methylbutadiene, but here the negative charge, instead of being displaced three carbon atoms away from the methyl hydrogens is displaced five carbons away to give



$$\mathrm{H{-}\underset{H}{\overset{H^+\ \ H}{C}}{=\!=}\overset{H}{C}{-}\overset{H}{C}{=}\underset{H}{\overset{H}{C}}{-}C:^-}$$

Since three such structures are the principal source of the moment of the molecule as in the cases of propylene and 2-methylbutadiene, the moment of the molecule should be to that of 2-methylbutadiene approximately as the charge separation in the 1-methyl is to that in the 2-methyl molecule. Measurement of the molecular models shows that the ratio of these distances is approximately 1.5 if 1-methylbutadiene is *cis* with respect to the central single bond and 1.8 if it has the more probable[8] *trans* structure. The fact that the ratio of the two moment values in Table II is 1.8 gives striking evidence in support of the validity of this theory of hyperconjugation as applied to unsaturated compounds.

Summary

The dielectric constants of the vapors of butadiene, 1-methyl-, 2-methyl- and 2,3-dimethylbutadiene have been measured and used to calculate the dipole moments of the molecules. The moment of 2,3-dimethylbutadiene shows that the molecules are largely, if not entirely, in a *cis* form with respect to the central C–C bond. The moment values give quantitative evidence in support of the theory of hyperconjugation, which requires positive charges on the methyl hydrogens and a negative charge on a terminal carbon.

PRINCETON, NEW JERSEY RECEIVED MAY 15, 1943

[COMMUNICATION NO. 940 FROM THE KODAK RESEARCH LABORATORIES]

Oxidation Processes. XVI.[1] The Autoxidation of Ascorbic Acid

BY A. WEISSBERGER, J. E. LUVALLE AND D. S. THOMAS, JR.

α-Ketols form with molecular oxygen the corresponding diketones and hydrogen peroxide

$$\mathrm{R{-}CHOH{-}CO{-}R + O_2 \longrightarrow R{-}CO{-}CO{-}R + H_2O_2}^{2} \quad (1)$$

The rates of this reaction and of the oxidation of α-ketols with Fehling solution[3] are *proportional to the hydroxyl-ion concentration of the solutions*, and it was suggested that the rate-determining phase is the enolization of the ketol to the enediol ion[2]

$$\mathrm{R{-}CHOH{-}CO{-}R + OH^- \rightleftarrows R{-}COH{=}CO^-{-}R + H_2O} \quad (2)$$

This suggestion was confirmed by the observation that under identical conditions of alkalinity, *d*-benzoin, in the absence of oxygen, is racemized at the *same rate* at which benzoin is oxidized, when shaken with oxygen.[4] When the oxygen supply is scant, an intensely colored intermediate appears, the free radical R—COH—CO—R.[2a] This indicates that the oxidation of the enolized compound proceeds in two steps[5] by way of the free radical. The ionic species reacting in the first step may be the monovalent ion, (3), or the divalent ion (4), which is formed in the equilibrium (5).

$$\mathrm{R{-}COH{=}CO^-{-}R + O_2(\text{or } O_2^-) \longrightarrow R{-}COH{-}CO{-}R + O_2^-(\text{or } O_2^{--})} \quad (3)$$

$$\mathrm{R{-}CO^-{=}CO^-{-}R + O_2(\text{or } O_2^-) \longrightarrow R{-}CO^-{=}CO{-}R + O_2^-(\text{or } O_2^{--})} \quad (4)$$

$$\mathrm{R{-}COH{-}CO^-{-}R + OH^- \rightleftarrows R{-}CO^-{=}CO^-{-}R + H_2O} \quad (5)$$

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(1) Part XV, Weissberger, Thomas and LuValle, THIS JOURNAL, 65, 1489 (1943).

(2) (a) Weissberger, Mainz and Strasser, *Ber.*, 62, 1942 (1929); (b) Weissberger, Strasser, Mainz and Schwarze, *Ann.*, 478, 112 (1930).

(3) Weissberger, Schwarze and Mainz, *Ann.*, 481, 68 (1930).

(4) Weissberger, Dörken and Schwarze, *Ber.*, 64, 1200 (1931); Weissberger and Dym, *Ann.*, 502, 74 (1933).

(5) Michaelis and Fletcher, THIS JOURNAL, 59, 1246 (1937).