the more complex carbethoxy and acetate groups. Since the assumption of free rotation about all single bonds is not justified in these cases, a more detailed analysis has not been attempted. From the moment of resorcinol diacetate reported here, and the literature values[4] for hydroquinone diacetate and *p*-cresyl acetate, the group moment (1.65) and angle (115°) may be found. Similarly a group moment (1.81) and angle (83°20′) were obtained for the carbethoxy group. Group moments used here are those considered appropriate for describing results obtained in benzene solution—with the exception of the carboxylate group moment which is derived from data obtained in dioxane solutions.

Acknowledgment.—The author is indebted to Mr. Morris Patapoff for the preparation of two compounds and for assistance in determining their electric moments.

EAST LANSING, MICHIGAN

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Electric Moments of Some Acetylenic Halides, Alcohols, Ethers and Amines

BY MAX T. ROGERS AND MORTON B. PANISH

RECEIVED FEBRUARY 15, 1955

The electric moments of propargyl bromide and iodide, and of several alkyl substituted derivatives of these, have been determined in benzene solution at 25°. The observed moments are in general lower than anticipated even when hyperconjugation is taken into account. If it is assumed that the acetylenic group is electron attracting, and leads to a reduction of 0.3 to 0.6 *D* in the carbon–halogen bond moment, reasonable calculated values are obtained. The electric moments of several acetylenic alcohols, ethers and amines are also reported and the values discussed.

Introduction

An electron diffraction investigation of a series of propargyl halides[1] showed that the carbon–halogen internuclear distances were longer than in the corresponding alkyl halides. To account for this observation it was postulated[1] that resonance structures of types I and II made a significant contribution to the ground state of the molecule. If this hypothesis were correct, the dipole moments of the propargyl halides should be about as large as, or larger than, those of the corresponding alkyl halides even when hyperconjugation is taken into account. We have, therefore, investigated the electric moments in benzene solution of a series of acetylenic halides; to extend the study the electric moments of some other acetylenic derivatives have been measured. No values have been reported previously for any of these substances, but the moments of propargyl bromide and propargyl alcohol had been determined by Rogers and Patapoff.[2]

$$\mathrm{H{-}C{\equiv}C{-}CH_2\overset{-}{Br}}$$

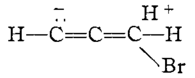
I

$$\mathrm{H{-}C{=}\overset{+}{C}{=}CH_2\overset{-}{Br}}$$

II

Results

The electric moment of propargyl bromide (1.49 *D*) may be compared with that of *n*-propyl bromide in benzene solution (1.95). If the moment of ethyl acetylene[3] (0.80) is used as a measure of the moment due to both hyperconjugation (structures of type III) and the difference in electronegativity between an acetylenic and normal carbon atom,[4] then the electric moments calculated for propargyl bromide and iodide are 1.85 and 1.80 *D*, respectively. The observed moments are lower by 0.35 and 0.60 *D*, respectively, and to account for the decrease it seems necessary to postulate that the carbon–halogen moments are lower in the propargyl halides. This could be attributed to an inductive effect, the acetylenic carbon atom being more electronegative than a normal carbon atom. We prefer to attribute it in a formal way to a resonance effect and consider that the contribution of structures such as IV and V to the ground state of the molecules is important.



III

$$\mathrm{H{-}C{\equiv}C{-}\overset{\overset{-}{..}}{C}H_2\overset{+}{Br}}$$

IV

$$\mathrm{H{-}\overset{\overset{-}{..}}{C}{=}C{=}CH_2\overset{+}{Br}}$$

V

A contribution of such structures equivalent to a decrease of 0.3 in the C–Br moment, or 0.6 in the C–I moment, reproduces the observed values when the hyperconjugation moment is also included. Since iodine has a lower ionization potential than bromine, the greater importance of structures IV and V in propargyl iodide is reasonable.

The effect becomes successively smaller as methyl groups are substituted for hydrogens on the carbon atom to which bromine is attached. Thus the moments of 2-bromo-3-butyne and 2-methyl-2-bromo-3-butyne are lower than calculated from the moments of the analogous alkyl halides (2-bromobutane and 2-bromo-2-methylbutane) and the hyperconjugation moment (0.8), but the differences, 0.16 and 0.13, are smaller than for the propargyl compound and indicate either a decreased contribution from structures analogous to IV and V or a decreased importance of hyperconjugation. If the reduction in the C–Br moment is taken to be 0.15, representing a

---

[1] L. Pauling, W. Gordy and J. H. Saylor, THIS JOURNAL, **64**, 1753 (1942).

[2] M. T. Rogers and M. L. Patapoff, unpublished results.

[3] L. G. Wesson, "Table of Electric Dipole Moments," The Technology Press, Cambridge, Mass., 1948; "Tables of Electric Moments of Substances in the Gaseous State," National Bureau of Standards Circular 537, Washington, D. C., 1953.

[4] See, for example, C. A. Coulson, "Valence," Oxford University Press, 1952.

contribution from structures IV and V of only one-half that in propargyl bromide, the observed and calculated values agree closely. There is some evidence[5] that hyperconjugation becomes less important when hydrogen atoms are replaced by methyl groups. The electric moment of 1-chloro-4-octyne is nearly equal to that of 1-chlorooöctane; this result would be expected since the hyperconjugation moments cancel and interaction between the chlorine atom and triple bond should be small.

It seems difficult to reconcile the dipole moment data with the lengthening of the carbon–halogen bonds. It has been suggested[6] that resonance with ionic structures such as IV and V may lead to lengthening of the bond distance for the same reasons that resonance with ionic structures of type I and II has been considered to lead to a lengthening of the internuclear distance.

The acetylenic alcohols studied have larger electric moments than the saturated alcohols, the moments of the latter in benzene solution being close to 1.66. The observed increase is satisfactorily accounted for in the case of propargyl alcohol by the vector addition of the hyperconjugation moment (0.8), and the moment (0.3) assigned to structures analogous to III and IV, to that of the saturated alcohol. The use of the same hyperconjugation moment leads to calculated values for 3-methyl-2-butyne-3-ol and 3-butyne-2-ol which are larger than observed. However, if the effect of hyperconjugation is assumed to decrease in importance with replacement of hydrogen atoms by methyl groups, the agreement is better. Thus, if there is no hyperconjugation in 3-methyl-2-butyne-3-ol, the calculated (1.64) and observed (1.59) values are within experimental error and, if the hyperconjugation moment is reduced to 0.4 in 3-butyne-2-ol, the calculated (1.65) and observed (1.69) values again agree within experimental error. The arguments are much weaker in the alcohol series since the effects are smaller than in the halide series, the assumption of free rotation has been made, and the omission (or inclusion) of the correction of 0.3 *D* to the C–O moment makes little difference to the calculated moment in many cases. The moment of 3-octyne-1-ol is 0.12 larger than the average of those of the saturated alcohols in benzene solution although it would be expected to be about the same since the hyperconjugation moment cancels and any interaction between the triple bond and hydroxyl group should be small.

The observed moment of propargyl ethyl ether (1.46) is somewhat higher than observed for saturated ethers[7] and higher than calculated by the method outlined above (1.28). It is possible that rotation about the C–O bond is not completely free, the ethyl and propargyl groups tending to be opposed. The observed moment of 1-diethylamino-2-propyne (0.80) is close to that of triethylamine (0.79) and lower than a value calculated (1.04) by vector addition of the moments, when both hyperconjugation and the contribution of structures analogous to III and IV are included. It is difficult to draw conclusions from the moments of the ethers and amines since the rather large contribution to the total moment made by the unshared electron pairs is very sensitive to small changes in bond angle and hybridization[4] (percentage *s* character in the bonds to oxygen or nitrogen).

The electric moments of the propargyl derivatives studied here are fairly well reproduced by adding to the moment of the saturated analog a hyperconjugation moment directed toward the triple bond, and an ionic moment directed from the halogen atom (or other substituent) to the carbon atom to which it is bonded. The agreement is improved if the hyperconjugation moment is assumed to decrease when methyl groups replace hydrogen atoms. There is no evidence for a significant contribution from structures analogous to I and II in these compounds; the acetylenic group appears to be an electron acceptor.

Experimental

Materials

Benzene.—Thiophene-free benzene was partially frozen and filtered; the crystals from a second such operation were melted and distilled from sodium, $d^{25}{}_{4}$ 0.89345.

Propargyl Bromide.—The sample of pure material used to obtain the data reported here was the gift of Prof. T. L. Jacobs, $n^{25}\text{D}$ 1.4900. A sample from Farchan Research Laboratories which had been dried and fractionated probably contained bromoallene,[8] $d^{25}{}_{4}$ 1.5657, $n^{25}\text{D}$ 1.4945. A sample synthesized from the chloride by refluxing with potassium bromide in acetone[2] was apparently fairly pure, $n^{25}\text{D}$ 1.4904, $d^{25}{}_{4}$ 1.5770. All three samples gave identical dipole moments since the moments of bromoallene and propargyl bromide are the same.[9]

Propargyl Alcohol.—Material from the Farchan Research Laboratories was dried and fractionated; $d^{25}{}_{4}$ 0.9436, $n^{25}\text{D}$ 1.4300. Propargyl alcohol which had been prepared synthetically gave the same electric moment[2]; $n^{25}\text{D}$ 1.4300, $d^{25}{}_{4}$ 0.9450.

3-Butyne-1-ol, 3-Butyne-2-ol, 2-Methyl-3-butyne-2-ol, 3-Octyne-1-ol.—Materials from the Farchan Research Laboratories were dried and fractionated through an efficient packed column; $d^{25}{}_{4}$ 0.9198, $n^{25}\text{D}$ 1.4393 (3-butyne-1-ol); $d^{25}{}_{4}$ 0.8890, $n^{25}\text{D}$ 1.4238 (3-butyne-2-ol); $d^{25}{}_{4}$ 0.8566, $n^{25}\text{D}$ 1.4240 (2-methyl-3-butyne-2-ol); $d^{25}{}_{4}$ 0.8767, $n^{25}\text{D}$ 1.4542 (3-octyne-1-ol).

Propargyl Iodide.—This was prepared by refluxing the bromide with sodium iodide. The product was dried and fractionated, $d^{25}{}_{4}$ 2.0214, $n^{25}\text{D}$ 1.5914. Comparison with physical constants quoted by Jacobs[8,10] suggests that our product is a mixture containing some but not a large proportion of iodoallene. Since the electric moments of iodoallene and propargyl iodide are probably nearly the same (the bromides are identical) the dipole moment reported here is probably not in error by more than 0.1 *D*.

Propargyl Ethyl Ether.—The alcohol was converted to the sodium salt by cautious addition of sodium, with cooling. Ethyl iodide was added and the mixture refluxed and fractionated. The crude material was refractionated, b.p. 80–81° (760 mm.), $d^{25}{}_{4}$ 0.8566, $n^{25}\text{D}$ 1.4240. There is no way to judge the purity of this material until the allene and propargyl derivatives have each been prepared in the pure state.

1-Chloro-4-octyne and 1-Diethylaminopropyne-2.—Materials from Farchan Research Laboratories were dried, distilled and fractionated; $n^{25}\text{D}$ 1.4551, $d^{25}{}_{4}$ 0.9329 (1-chloro-4-octyne); $d^{25}{}_{4}$ 0.7982, $n^{25}\text{D}$ 1.4291 (1-diethylaminopropyne-2).

2-Bromo-3-butyne.—This was prepared in low yield by adding phosphorus tribromide to a slight excess of the 3-butyne-2-ol (Farchan Laboratories) at −15° in the presence of

---

(5) J. W. Baker, "Hyperconjugation," Oxford University Press, 1952.

(6) V. F. H. Schomaker, private communication.

(7) R. A. Spurr and H. Zeitlin, THIS JOURNAL, **72**, 4832 (1950).

(8) T. L. Jacobs and W. F. Brill, *ibid.*, **75**, 1314 (1953).

(9) M. T. Rogers, unpublished results.

(10) T. L. Jacobs, private communication.

TABLE I

EMPIRICAL CONSTANTS AND MOLAR POLARIZATIONS IN BENZENE SOLUTION AT 25°, MOLAR REFRACTIONS AND DIPOLE MOMENTS

	ϵ_1	a	v_1	b	P_2	MR_D, obs.	Obsd.	Calcd.
3-Bromopropyne-1 (propargyl bromide)	2.2718	3.08	1.14500	−0.778	67.74	22.14	1.49	1.57
3-Iodopropyne-1 (propargyl iodide)	2.2720	2.20	1.14460	−1.335	57.86	27.76	1.21	1.23
2-Bromobutyne-3	2.2730	4.21	1.14450	−0.700	90.97	27.18	1.76	1.71
2-Methyl-2-bromobutyne-3	2.2724	5.02	1.14440	− .640	109.0	32.00	1.94	1.84
1-Chloroöctyne-4	2.2730	4.85	1.14480	− .140	117.3	42.08	1.92	1.85
2-Propyne-1-ol (propargyl alcohol)	2.2725	4.25	1.14440	− .043	80.54	15.35	1.78	1.77
3-Butyne-1-ol	2.2700	3.91	1.14450	+ .007	81.30	20.02	1.73	1.82
3-Butyne-2-ol	2.2720	3.66	1.14490	+ .020	78.20	20.11	1.69	1.77
2-Methyl-3-butyne-2-ol	2.2722	3.13	1.14490	+ .090	76.78	25.05	1.59	1.77
3-Octyne-1-ol	2.2720	4.12	1.14480	+ .010	103.8	39.00	1.78	1.66
Propargyl ethyl ether	2.2725	2.54	1.14480	+ .080	67.87	24.45	1.46	1.28
1-Diethylaminopropyne-2	2.2725	0.50	1.14490	+ .170	49.21	36.07	0.80	1.10

A hyperconjugation moment of 0.8, and $\overset{-}{\mathrm{C}}\text{–}\overset{+}{\mathrm{X}}$ moment of 0.3 have been added vectorially to the moment of the corresponding saturated derivative in benzene solution. By using the moment of the corresponding saturated derivative as the basis of each calculation ordinary inductive effects are to a large extent allowed for.

pyridine. The reaction mixture was washed with water, the organic layer removed, dried with calcium chloride, and fractionated; $d^{25}{}_4$ 1.3815, $n^{25}{}_D$ 1.4766. No product was obtained when thionyl bromide replaced the phosphorus tribromide.

2-Methyl-2-bromobutyne-3.—Dry hydrogen bromide was passed through[11] pure 2-methyl-3-butyne-2-ol at 0° as long as it was absorbed. The organic layer was washed with water, neutralized and dried over potassium carbonate (all at 0°). The crude product was fractionated under reduced pressure; $n^{25}{}_D$ 1.4631, $d^{25}{}_4$ 1.2657.

Method

The dielectric constants and densities of six benzene solutions of each compound, ranging from 0.001 to 0.020 mole fraction solute, were determined at 25°. The apparatus, technique and method of calculation have been described in a previous publication[12] and the symbols used there have been retained. The electric moments were calculated from the observed molar refractions, and from the molar polarizations of the solutes derived by the method of Halverstadt and Kumler.[13] The constants ϵ_1, v_1, a and b of their equation and the values of the molar polarization of the solute at infinite dilution P_2 for each compound are shown in Table I along with the observed molar refractions MR_D and the calculated dipole moments μ. The probable error in the dipole moment is about ±0.05 D.

Acknowledgment.—The authors are indebted to Professor Thomas L. Jacobs for the gift of a sample of pure propargyl bromide and to Mr. M. Patapoff for preliminary work on this problem.

EAST LANSING, MICHIGAN

---

[11] K. N. Campbell and J. T. Ely, THIS JOURNAL, **62**, 1798 (1940).

[12] M. T. Rogers, *ibid.*, **77**, 3681 (1955).

[13] I. F. Halverstadt and W. D. Kumler, *ibid.*, **64**, 2988 (1942).

[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE COLLEGE]

The Electric Moments of Some Fluorocarbon Derivatives

BY MAX T. ROGERS AND RICHARD D. PRUETT

RECEIVED FEBRUARY 15, 1955

The electric moments of perfluoroethyl ether, perfluorotetramethylene oxide, chlorotrifluoroethylene and 1,1,2,2,3,3,3-heptafluoropropane have been determined from measurements of the dielectric constants of the gases at several temperatures. The electric moments of perfluorotriethylamine and ethyl perfluorobutyrate were measured in benzene solution at 25°. The observed moments of the ethers are close to the values calculated by use of bond moments but the amine and ester have larger moments than calculated. The values have been discussed and compared with moments calculated on the basis of reasonable models for the molecules.

The physical properties of completely fluorinated ethers and amines suggest that these compounds are less polar than the normal amines and ethers and that the lone-pair electrons are less available for coördination with an acid.[1] Since the electric moments of these compounds should provide information concerning their electronic structures, we have measured the moments of two perfluoroethers and a perfluoroamine and have compared the results with the corresponding hydrogen compounds. To obtain a value for the difference between the C–H and C–F bond moments for use in the calculations, a measurement of the moment of 1,1,2,2,3,3,3-heptafluoropropane was made.

Results

The electric moment of 1,1,2,2,3,3,3-heptafluoropropane, 1.62, is somewhat lower than that of n-amyl fluoride (1.85).[2] The decrease is analogous to that observed in going from methyl fluoride (μ = 1.808) to fluoroform[3] (μ = 1.645) and may be attributed to larger inductive effects in the compounds with many fluorine atoms. If the C–H moment is taken to be 0.4 D, with hydrogen positive, then the C_3F_7 group moment is 1.22 D.

A moment may then be calculated for perfluorodiethyl ether or perfluorotetramethylene oxide by replacing the C_2H_5 group moment (0.4) by the

---

[1] J. H. Simons, Ed., "Fluorine Chemistry," Academic Press, Inc., New York, N. Y., 1950, Chap. 14.

[2] M. T. Rogers, THIS JOURNAL, **69**, 457 (1947).

[3] "Tables of Electric Dipole Moments of Substances in the Gaseous State," Bureau of Standards Circular 537, Washington, D. C., 1953.