caused to react with the addition product resulting from interaction of another Grignard reagent with a nitrile.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Structural Effects of Unsaturation and Hyperconjugation in Aldehydes, Nitriles and Chlorides as Shown by their Dipole Moments in the Vapor State

BY EVERETT C. HURDIS AND CHARLES P. SMYTH

Formaldehyde has hitherto been the only first member of an important homologous series, the dipole moment of which has not been determined. In spite of the difficulties created by its ease of polymerization, it has, therefore, seemed desirable to investigate it and higher members of its series in order to study the effects of induction and resonance in the series. The part played by unsaturation in such effects was then studied by measuring crotonaldehyde and the investigation was extended to the unsaturated nitriles. Because of the similarity of chloride to nitrile, isocrotyl chloride was measured. The results of measurements upon diketene vapor carried out in connection with the question of its structure are included because of its relation to the aldehydes.

The dielectric constants of the vapors were measured with the apparatus and technique previously described.[1–4] The measurements were made by the "extrapolation method," in which the effects of deviations from the gas laws were eliminated by measurement over a wide range of pressure, or 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[4] of values established by other work. It is close to the relative accuracy evident in the data in Table I.

Preparation and Purification of Materials

Formaldehyde.—Monomeric liquid formaldehyde was prepared by the method of Spence and Wild[5] in an all-glass generator connected to the gas apparatus.

Acetaldehyde.—Material from the General Chemical Company was purified by fractional distillation under vacuum in an all glass trap system connected to the gas apparatus.

Propionaldehyde.—Material from the Paragon Testing Laboratories was dried over calcium chloride and fractionally distilled in an atmosphere of nitrogen, b. p. 47.6° (748 mm.).

***n*-Butyraldehyde.**—Material from the Paragon Testing Laboratories was fractionally distilled in an atmosphere of nitrogen, b. p. 74.4° (741 mm.).

Crotonaldehyde.—Material from the Paragon Testing Laboratories was fractionally distilled in an atmosphere of nitrogen, b. p. 101.0° (743 mm.).

Diketene.—Material which had been purified by distillation and re-crystallization was very kindly given us by Dr. F. O. Rice of Catholic University.

Propionitrile.—Two hundred grams of material from the Eastman Kodak Company was dried over calcium chloride and fractionally distilled, b. p. 96.9° (747 mm.).

Acrylonitrile.—Two hundred grams of material from the American Cyanamid Company was dried over calcium chloride and fractionally distilled, b. p. 77.3° (750 mm.); n^{22}_{D} 1.3907; density at 22°, 0.8076.

***trans*-Crotononitrile.**—Crotonaldoxime was prepared from crotonaldehyde by the method of Schindler.[6] Dehydration of the oxime according to Dollfus[7] resulted in 37 g. of material boiling between 114 and 124°. This sample was fractionally distilled in a column of fourteen theoretical plates and the main fraction (18 g.) with boiling range 120.1 to 120.9° (762 mm.) was used for the measurements. Density at 22° was 0.8183, n^{22}_{D} 1.4214, MR^{22}_{D} 20.79. Heim[8] gives b. p. 122.0° (755 mm.), MR^{15}_{D} 20.75, MR^{30}_{D} 20.81. (The *cis* form boils at 107.5°.)

Iso-crotyl Chloride.—Two hundred grams of material from the Eastman Kodak Company was fractionally distilled in a column of 14 theoretical plates; b. p. 66.9° (757 mm.); density at 25°, 0.9144; n^{25}_{D} 1.4198.

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

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[1] McAlpine and Smyth, THIS JOURNAL, **55**, 453 (1933).

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

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

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

[5] Spence and Wild, *J. Chem. Soc.*, 338 (1935).

[6] Schindler, *Sitzber. Akad. Wiss. Wien Math.-naturw. Klasse*, **100**, II-B, 361 (1891).

[7] Dollfus, *Ber.*, **25**, 1920 (1892).

[8] Heim, *Bull. soc. chim. belg.*, **42**, 461 (1933).

TABLE I

POLARIZATIONS AND DIPOLE MOMENTS

T, °K.	P		P_{av}	$\mu \times 10^{18}$
Formaldehyde				
420.4	82.3	83.2	81.8	2.27
	79.9			
463.9	75.2	76.2	75.8	2.29
	76.6	75.4		
498.3	72.8	69.7	70.1	2.27
	66.7	71.6		
	70.2	69.7		
519.6	66.5	67.2	66.4	2.25
	65.4	66.4		
Acetaldehyde				
420.3	118.5	119.4	118.5	2.72
	116.5	119.2		
	118.7			
468.6	109.2	107.0	108.6	2.73
	108.2	109.4		
	109.2	108.4		
Propionaldehyde				
354.3	143.4	143.5	143.4	2.72
	142.6	144.0		
	143.7			
390.9	133.2	132.1	132.4	2.73
	131.7	131.2		
	133.4			
431.1	119.5	120.2	121.1	2.73
	122.7	120.5		
	122.4			
468.3	110.7	112.3	112.2	2.72
	112.4	112.8		
	112.8			
509.2	104.0	105.6	105.2	2.73
	107.8	103.5		
	103.8	106.2		
n-Butyraldehyde				
354.3	147.0	149.3	147.8	2.72
	146.8	147.7		
	147.1	149.0		
387.1	136.0	138.7	136.9	2.72
	136.0	136.7		
	137.7	136.2		
	136.7	137.4		
411.8	131.0	130.3	130.8	2.73
	129.9	131.5		
	129.4	131.1		
	132.2			
Crotonaldehyde				
411.8	219.1	219.4		3.65 3.66
432.9	207.8			3.64
457.3	203.5	205.1		3.70 3.71
463.3	200.2			3.69
473.3	195.2			3.67
485.6	192.0			3.68
507.1	182.7			3.66
519.3	175.7	176.5		3.63 3.64
Diketene				
432.8	197.2	197.2	194.8	3.52
	193.2	191.8		
471.8	180.1	181.8	180.6	3.53
	180.1	180.2		
515.5	166.9	166.7	167.9	3.54
	170.0			
Propionitrile				
395.1	265.2	260.1		4.02 3.98
420.1	244.0	253.8		3.97 4.05
476.8	218.2	219.4		3.98 3.99
Acrylonitrile				
386.5	251.8			3.87
402.7	242.2			3.87
427.4	230.0			3.88
453.7	217.3			3.88
476.8	207.5	207.5		3.88 3.88
509.3	196.1	196.3		3.89 3.89
trans-Crotononitrile				
408.7	322.6	328.0	324.3	4.51
	327.7	319.0		
	324.3			
451.9	288	294	292.8	4.49
	294	295		
516.1	261	257	259.0	4.49
Iso-crotyl Chloride				
357.5	90.4	94.0	91.8	1.98
	91.0	91.8		
399.5	86.5	83.8	85.7	1.99
	86.1	85.0		
	86.5	86.3		
453.3	78.1	77.0	78.0	1.99
	81.8	76.9		
	77.1	77.0		
522.7	68.8	68.1	71.1	1.99
	71.2	74.8		
	70.6	71.0		
	73.5			

TABLE II

MOLAR REFRACTIONS AND MOMENT VALUES

	MR_D	$\mu \times 10^{18}$
Formaldehyde	7.0[a]	2.27
Acetaldehyde	11.6[b]	2.72
Propionaldehyde	16.0[b]	2.73
n-Butyraldehyde	20.6[b]	2.72
Crotonaldehyde	21.5[b]	3.67
Diketene	20.1[c]	3.53
Propionitrile	15.8[b]	4.00
Acrylonitrile	15.6[d]	3.88
trans-Crotononitrile	20.8[d,e]	4.50
Iso-crotyl chloride	25.0[a,d]	1.99

[a] Calculated from refractions in Landolt–Börnstein (fifth edition). [b] Landolt–Börnstein (fifth edition). [c] Measured by Chick and Wilsmore, *J. Chem. Soc.*, **93**, 946 (1908). [d] Measured in this Laboratory. [e] Measured by Heim, *Bull. soc. chim. belg.*, **42**, 461 (1933).

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.

Considerable difficulty in measuring the vapor phase moment of formaldehyde might be anticipated, due to the readiness with which it polymerizes. However, Trautz and Ufer[9] showed that the vapor obtained from liquid formaldehyde obeys the gas laws and is actually monomeric formaldehyde. Furthermore, the polymerization of gaseous formaldehyde appears to take place only heterogeneously to give a high molecular weight solid polymer, and there is no evidence of the formation of intermediate polymerides of low molecular weight in the gas phase.[10] Thus it appears that if liquid formaldehyde is prepared and the vapor introduced into a dielectric cell, it should be possible to obtain the polarization of the monomeric gas. A possible interference would arise from deposition of solid polymer on the plates of the cell itself, thus giving a continually varying capacity. Since, however, the solid polymers of formaldehyde decompose rapidly at 130° to give the gas, this error can be avoided by making measurements at 130° or higher. No difficulty was experienced, under the conditions chosen for measurement, with formation of polymer in the cell, but the first attempts at measurement were quite unsuccessful because of deposition of solid polymer in the cool parts of the vacuum system. This deposition took place at such a rate that the pressure of vapor in the cell could not be held even approximately constant, and, furthermore, clouding of the manometer by the polymer made it impossible to determine accurately the height of the meniscus. To remove this source of error, the entire vacuum system was heated by a wrapping of nichrome wire to a temperature at which the polymer had a vapor pressure of about 100 mm. and was formed only very slowly. Under these conditions it was necessary to use a high-temperature stopcock grease made of mannitol, dextrose and glycerol. Since polymerization was faster at higher pressures, the two-point method was used for the determinations, capacity readings being taken at 10–20 mm. and at 200–300 mm. At a given pressure the capacity was first measured, then the pressure, and the capacity again, the two capacity readings being averaged for calculation of the dielectric constant. If one of the capacity values, instead of the average, had been used for calculation, the moment obtained would very seldom have been changed by more than 0.01 to 0.03. Averaged moments determined in this way were in good agreement for four temperatures, covering a range of 99°.

The moments of acetaldehyde, propionaldehyde and *n*-butyraldehyde were also measured by the two-point method, no difficulty due to polymerization being experienced for these compounds. The moment obtained for acetaldehyde, 2.72×10^{-18}, is identical with the value recalculated on the basis of the molar refraction from the polarizations determined by Zahn.[11]

Because propionaldehyde gave consistent moment results over a wide range of temperature (155°), its moment was calculated from a plot of polarization against the reciprocal of the absolute temperature, as well as by the optical method. The plot gave a good straight line, the slope of which led to a moment of 2.71, as compared with 2.73 based on the refraction. The intercept on the polarization axis was 17.7, indicating a total induced polarization 1.7 units higher than MR_D. The moment of acrylonitrile was measured by the extrapolation method over a range of 123°, the average moment based on MR_D being 3.88. A plot of P against $1/T$ made for this compound gave a total induced polarization of 20.0, 4.3 units higher than the molar refraction. The moment calculated from the slope of the line is 3.84. The rather high value of the atomic polarization indicated by the plot may be due in part, at least, to the error involved in the long extrapolation.

Discussion of Results

The moment of acetone has previously been used[12] to calculate a bond moment 2.5 for the carbonyl bond. For use in molecular moment calculations, there seems to be no reason to change this calculation, but, for examination of a carbonyl group with a minimum of environmental influence, the moment of formaldehyde, 2.27, given in Table II, provides a more satisfactory basis for calculation. If the moment of the H–C bond is taken[13] as 0.3, the carbonyl bond moment comes out 2.0, while the assignment of 0.4 to the H–C bond gives 1.9 for the carbonyl bond. Since

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[9] Trautz and Ufer, *J. prakt. Chem.*, **113**, 105 (1926).

[10] Spence, *J. Chem. Soc.*, 1193 (1933).

[11] Zahn, *Physik. Z.*, **33**, 686 (1932).

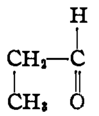
[12] Smyth, THIS JOURNAL, **60**, 183 (1938).

[13] Smyth, *J. Phys. Chem.*, **41**, 209 (1937).

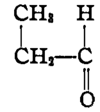
calculation of the acetone moment by the use of molar refraction gives a value 0.6 higher than that of formaldehyde, it may be stated that the carbonyl bond moment value obtained from the latter is 0.6 lower.

The moment of formaldehyde is 0.45 lower than that determined for acetaldehyde, while the moment of acetone, recalculated from the polarizations of Zahn,[11] is 0.16 higher. It is seen that the rise produced by substituting the first methyl group in formaldehyde is markedly greater than that produced by the introduction of the second methyl group. A rough calculation of the moment induced in the methyl group by the dipole in the carbon–oxygen bond gives a moment rise from formaldehyde to acetaldehyde close to that observed. In view of the extremely approximate character of any such calculation, which may easily give an absolute error of more than 50%, it is, perhaps, more significant that the ratio of the calculated rise from formaldehyde to acetone to that from formaldehyde to acetaldehyde is close to the observed. The fact that the second methyl group affects the calculated rise much less than the first is due to the cancellation of the component of moment induced in one methyl group perpendicular to the direction of the carbonyl group axis by the component in the other methyl group. A second factor which must make an important contribution is the existence of resonating polar structures, which will be discussed presently. The significance of the resonance forms is that the methyl group can furnish electrons to the C–O bond because of partial ionic character in the C–H bonds, while that of the inductive effect is rather that the positive charge on the carbonyl carbon displaces the whole electronic shell of the methyl group carbon slightly, so as to raise the resultant moment.

It is interesting to note that the moments of acetaldehyde, propionaldehyde and *n*-butyraldehyde are identical within the experimental error. This result differs from that of the solution measurements of Coomber and Partington,[14] who reported an increase of 0.05 from the moment of acetaldehyde to that of propionaldehyde and a further increase of 0.03 from propionaldehyde to *n*-butyraldehyde. The solvent-effect lowering indicated by their measurements is of about the expected magnitude, however, being 0.23 for acetaldehyde and 0.19 for propionaldehyde. The absence of moment increase shown by the gas values for lengthening of the carbon chain beyond the two carbons of acetaldehyde parallels a similar absence of appreciable increase in the solution values of the ketones[15] and in the gas values of the nitroparaffins[4,16] beyond nitroethane. If the large increase in moment from formaldehyde to acetaldehyde arose wholly from induction, one might expect so large an effect to produce a further increase from acetaldehyde to propionaldehyde. The absence of this increase may be regarded as an indication that, as previously indicated, the increase from formaldehyde to acetaldehyde is not caused wholly by induction, but, in part, by resonance, a fact to be discussed shortly. Another factor is that of molecular shape. A molecular model of propionaldehyde shows that, when the carbonyl oxygen is nearest the methyl group in a *cis*-position



to give a maximum inductive effect, the moment induced in the methyl would partially oppose that of the carbonyl dipole and tend to decrease the total moment. In a *trans*-position



the carbonyl dipole would be relatively remote from the methyl group, which would thus tend to increase the total moment by only a small amount. Approximate compensation of inductive effects could thus occur as suggested in the case of the alcohols,[17] and could be a factor in preventing increase of moment with increase in the number of carbon atoms beyond two.

The dipole moment of crotonaldehyde was measured, by the extrapolation method, in order to obtain a check on the solution value of Bentley,[18] 3.54×10^{-18}, a value surprisingly high in comparison with that of acrolein, 2.88,[14] since crotonaldehyde differs from acrolein only in having a methyl group substituted on the β-carbon atom. However, measurement of the vapor

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[14] Coomber and Partington, *J. Chem. Soc.*, 1444 (1938)

[15] Fuchs and Wolf, "Hand- und Jahrbuch der chemischen Physik," (Eucken and Wolf) Vol. VI, Akademische Verlagsgesellschaft, Leipzig, 1935, p. 360.

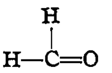
[16] Wiswall and Smyth, *J. Chem. Phys.*, 9, 356 (1941).

[17] Smyth, THIS JOURNAL, 63, 57 (1941).

[18] Bentley (unpublished) quoted on page xl, *Trans. Faraday Soc.*, 30, Appendix (1934).

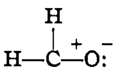
gave a result, 3.67, in good agreement with the value of Bentley, being 0.13 higher. (The gas moment of *n*-butyraldehyde is 0.15 higher than the solution moment.) The dipole moment of crotonaldehyde may, therefore, be taken to be 0.95 higher than that of *n*-butyraldehyde, the corresponding saturated compound, a difference which must be due largely to resonance.

The large moment of the carbonyl bond has been attributed to a large contribution from a polar structure. On this basis, the principal structures of formaldehyde would be



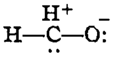
$\mathrm{H{-}\overset{\overset{\textstyle H}{|}}{C}{=}O}$

and



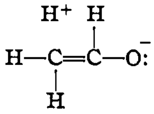
$\mathrm{H{-}\overset{\overset{\textstyle H}{|}}{C}{\overset{+}{-}}\overset{-}{O}{:}}$

The introduction of the idea of a variable amount of ionic character in the H—C bond as in the cases of chloroform and chloronitroparaffins[4] would give two structures such as



$\mathrm{H{-}\overset{H^+}{C}{-}\overset{-}{\underset{\cdot\cdot}{O}}{:}}$

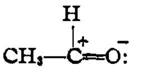
For acetaldehyde, in addition to three structures analogous to the three written for formaldehyde, three structures may be written of the type



$\mathrm{H{-}\underset{\underset{\textstyle H}{|}}{\overset{H^+}{C}}{=}\overset{\overset{\textstyle H}{|}}{C}{-}\overset{-}{O}{:}}$

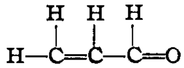
Evidence of contributions from such structures is given by the shortening of the C—C bond by 0.04 below the length of the normal single C—C bond found by means of electron diffraction.[19]

The use of Pauling's relation between bond-shortening and amount of double bond character[20] gives about 8% as the amount of double bond character in this bond. In other words, the total contribution of these three highly polar structures to the acetaldehyde structure is about 8%. This should cause a large rise in moment from formaldehyde to acetaldehyde, as observed. That the moment rise is not even larger is probably due to the fact that the contributions from these highly polar structures, presumably, replace, in part, contributions from the polar structure



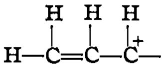
$\mathrm{CH_3{-}\overset{\overset{\textstyle H}{|+}}{C}{=}\overset{-}{O}{:}}$

The solution value of acrolein is 0.39 higher than that of acetaldehyde, and the gas value, that is, the true molecular moment value, would, therefore, be close to 3.11. The large increase of moment produced by the presence of the double bond may be attributed to the ease of transfer of charge through a double bond. The normal structures of acrolein would be



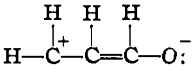
$\mathrm{H{-}\overset{\overset{\textstyle H}{|}}{C}{=}\overset{\overset{\textstyle H}{|}}{C}{-}\overset{\overset{\textstyle H}{|}}{C}{=}O}$

and



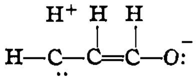
$\mathrm{H{-}\overset{\overset{\textstyle H}{|}}{C}{=}\overset{\overset{\textstyle H}{|}}{C}{-}\overset{\overset{\textstyle H}{|+}}{C}{-}O{:}^-}$

There would be, in addition, polar structures with ionic hydrogen analogous to those written for acetaldehyde. While the replacement of a methyl hydrogen in acetaldehyde by a methyl group does not increase the moment of propionaldehyde, the conjugation of the acrolein molecule facilitates the transmission of charge to the negative oxygen by means of contributions from structures such as



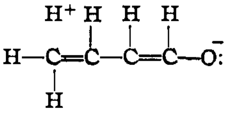
$\mathrm{H{-}\overset{\overset{\textstyle H}{|+}}{C}{-}\overset{\overset{\textstyle H}{|}}{C}{=}\overset{\overset{\textstyle H}{|}}{C}{-}\overset{-}{O}{:}}$

and



$\mathrm{H{-}\underset{\cdot\cdot}{\overset{H^+}{C}}{-}\overset{\overset{\textstyle H}{|}}{C}{=}\overset{\overset{\textstyle H}{|}}{C}{-}\overset{-}{O}{:}}$

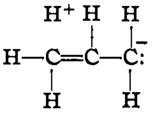
The effect of hyperconjugation[21] is shown more strikingly in the surprisingly large rise in moment, nearly 0.6, resulting from the replacement of an end hydrogen in acrolein by a methyl group to form *trans*-crotonaldehyde. In addition to polar structures analogous to those which have been proposed for acrolein, one can write for crotonaldehyde three highly polar structures such as



$\mathrm{H{-}\underset{\underset{\textstyle H}{|}}{\overset{H^+}{C}}{=}\overset{\overset{\textstyle H}{|}}{C}{-}\overset{\overset{\textstyle H}{|}}{C}{=}\overset{\overset{\textstyle H}{|}}{C}{-}\overset{-}{O}{:}}$

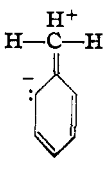
the apparent stability of which should tend to increase the moment, as observed.

Polar structures analogous to those which have been written for the aldehydes account for the moments of propylene, 0.35, α-butylene, 0.37, and toluene, 0.36. Thus, three structures may be written for propylene of the type

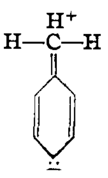


$\mathrm{H{-}\underset{\underset{\textstyle H}{|}}{\overset{H^+}{C}}{=}\overset{\overset{\textstyle H}{|}}{C}{-}\underset{\underset{\textstyle H}{|}}{\overset{\overset{\textstyle H}{|-}}{C}}{:}}$

and nine structures may be written for toluene of the types



and



The low moments found for the molecules show

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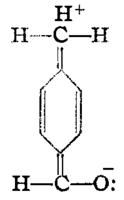
[19] Stevenson, Burnham and Schomaker, THIS JOURNAL, 61, 2922 (1939).

[20] Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 175.

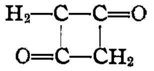
[21] Mulliken, Rieke and Brown, THIS JOURNAL, 63, 41 (1941).

that the contributions of these polar structures are small and their stabilities, therefore, low. The presence of the strongly negative oxygen in the aldehydes tends to stabilize the polar structures, and, consequently, increase their contributions to the structures of the molecules. This effect is detectable in the aromatic aldehydes as well as in the aliphatic, which have been considered. Benzaldehyde has a solution value for its moment 0.2 higher than those of the higher aliphatic aldehydes according to the measurements of Williams[22] and Goebel and Wenzke,[23] while, according to Coomber and Partington,[14] its moment is about 0.4 higher. Measurement by the two-point method at a single temperature, 462.8°K., gave a vapor value, 3.16, in agreement with the solution value of Coomber and Partington when allowance is made for the lowering of the latter value by solvent effect As these measurements were not extended, their result is too tentative for inclusion in Tables I and II. Goebel and Wenzke attribute the higher moment of the aromatic compound to contributions from the three generally accepted polar forms in which an electron pair has shifted from an ortho or a para carbon and to the oxygen, the carbonyl carbon being connected by a double bond to the ring. The two structures with the shift from the ortho carbon are closely analogous to the third structure written above for acrolein. The effect of hyperconjugation which contributes to the moment rises in acrolein and crotonaldehyde should raise the moment of the conjugated system of *p*-tolualdehyde, for which, in addition to polar structures analogous to those mentioned for benzaldehyde and for toluene, three structures may be written of the type



The moment calculated for *p*-tolualdehyde from the lower value for benzaldehyde and the moment of toluene is 2.99 as compared to 3.30 observed in solution,[24] and that calculated from the higher value for benzaldehyde reported by Coomber and Partington would still be appreciably lower than the observed. This small increase in moment above the calculated value gives evidence of the existence of small contributions from polar structures of the type shown. Here, as in the aliphatic aldehydes, though to a lesser extent, the presence of the negative oxygen tends to stabilize the polar structures containing ionic hydrogen.

The dipole moment of diketene was previously measured[25] in benzene solution. The value obtained, 3.31, was considered to invalidate two of the six previously proposed structures. However, recent work on the pyrolysis of gaseous diketene by Dr. F. O. Rice of Catholic University (private communication) seemed to indicate as correct the previously eliminated cyclobutadione structure



It is reasonable to suppose that the cyclobutane ring in this structure would be planar, especially since Bauer and Beach[26] have concluded from electron diffraction studies that the cyclobutane ring is planar in methylenecyclobutane. This being the case, the cyclobutadione structure should have zero dipole moment, a considerable contrast with the value, 3.31, found in benzene solution. However, it was considered possible that gaseous diketene existed in the cyclobutadione structure, but that solution in benzene caused enolization to a structure which should have a moment close to that observed. The gas value given in Table II is 3.53, 0.22 higher than the solution value. As this solvent effect is about what would be expected for a molecule of this type, it appears that diketene has the same structure in solution as in the gas. The gas and solution moments seem to be irreconcilable with the cyclobutadione structure for diketene.

The increase from the moment of hydrogen cyanide, 2.93, to that of acetonitrile, 3.94, is analogous to that from formaldehyde to acetaldehyde, though larger, and, as in their case, presumably, arises, in part, from induction and, in part, from contributions from analogous polar structures. For hydrogen cyanide, we may write

$$\mathrm{H{-}C{\equiv}N}\qquad \mathrm{H{-}CN}\overset{+\ \ -}{=}\!:\qquad \mathrm{H^{+}\ddot{C}{=}N\!:^{-}}$$

The contributions of the two polar structures are responsible for the large moment of the molecule and the different character of the H–C bond from that in hydrocarbons. Two structures analogous

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[22] Williams, THIS JOURNAL, **52**, 1993 (1930).

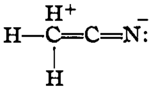
[23] Goebel and Wenzke, *ibid.*, **59**, 2301 (1937).

[24] Pearce and Berhenke, *J. Phys. Chem.*, **39**, 1005 (1935).

[25] Oesper and Smyth, THIS JOURNAL, **64**, 768 (1942).

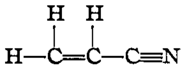
[26] Bauer and Beach, *ibid.*, **64**, 1142 (1942).

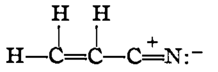
to the first two for hydrogen cyanide may be written for acetonitrile and, in addition, three highly polar structures of the type

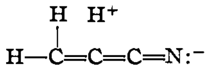

$\mathrm{H{-}\overset{H^+}{\underset{H}{C}}{=}C{=}\overset{-}{N}:}$

Indication of the contributions from such structures is given by the shortening of the carbon–carbon bond by 0.05 Å. shown by electron diffraction measurements.[27] The greater contribution from these polar structures as compared to those from analogous structures in acetaldehyde indicated by the greater moment rise is in accord with the conclusion of Pauling, Springall and Palmer[27] "that a double bond or aromatic nucleus is much less effective than a triple bond in changing the properties of an adjacent carbon–hydrogen bond."

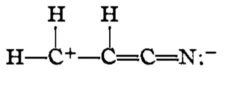
The moment value, 4.00, for propionitrile in Table II is close to the value 4.04 reported by Groves and Sugden.[28] The small rise from the methyl to the ethyl compound, which is intermediate between the zero rise for the aldehydes and the rise of 0.2 for the nitroparaffins, can be due to induction. In view of the fact that acrolein has a moment nearly 0.4 higher than propionaldehyde, it is surprising to find the moment of acrylonitrile 0.12 lower than that of propionitrile. For acrylonitrile, one may write structures analogous to those for acetonitrile

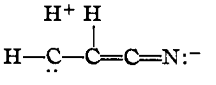

$\mathrm{H{-}\overset{H}{C}{=}\overset{H}{C}{-}C{\equiv}N}$


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

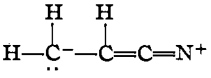

$\mathrm{H{-}\overset{H}{C}{=}\overset{H^+}{C}{=}C{=}N:^-}$

and, in addition, structures characteristic of the conjugated system, as in the case of acrolein

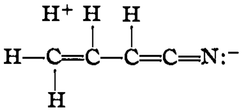

$\mathrm{H{-}\overset{H}{C}^+{-}\overset{H}{C}{=}C{=}N:^-}$


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

Another structure, which was not written in the case of acrolein because there was no indication of a contribution from it and the greater electronegativity of oxygen as compared to nitrogen would make it more unstable than in the present case, may be written


$\mathrm{H{-}\overset{H}{\underset{\cdot\cdot}{C}}^-{-}\overset{H}{C}{=}C{=}N^+}$

Although it might be expected that the electronegativity of nitrogen would reduce the stability of this structure with a positively charged nitrogen atom, it must be remembered that the nitrogen atom of the isocyanide group also carries a positive charge. The lower moment of acrylonitrile as compared to propionitrile indicates the probability of a contribution from this structure with positive nitrogen sufficiently large to overcome the rise in moment produced by the contributions from structures such as the fourth and fifth with negative nitrogen. The replacement of an end hydrogen by a methyl group in going from acrylonitrile to crotononitrile produces almost the same sharp rise in moment, 0.6, as the similar change in the aldehydes, indicating, as in the case of the aldehydes, the comparative stability of highly polar structures such as


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

Stabilization, through hyperconjugation, of these structures, which should have practically the same moment for the aldehyde as for the nitrile, produces practically the same rise in moment. The solution moment values of *p*-methylbenzonitrile and *p*-nitrotoluene are about 0.1 above those calculated as the sums of the component moments, indicating probable small contributions to their molecular structures from polar structures analogous to those proposed for *p*-tolualdehyde, but determinations in the vapor state are not yet available to confirm this.

Both acrylonitrile and crotononitrile show values of MR_D appreciably higher than those calculated from atomic refractivities, an exaltation due to conjugation of the carbon–carbon double bond with the carbon–nitrogen triple bond. It would appear that the exaltation for crotononitrile (0.82) is greater than that for acrylonitrile (0.31) because the added resonance in crotononitrile gives a considerable increase in the mobility of the resonance electrons. A similar effect is shown by acrolein (exaltation, 0.62) and crotonaldehyde (exaltation, 1.36).

The lowering of moment of vinyl chloride,[29] 1.44, as compared to that of ethyl chloride, 2.05, is much greater than that from propionitrile to acrylonitrile, but is attributable to a similar cause,[29] contribution from a structure with double bonded, positive chlorine

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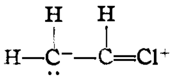
[27] Pauling, Springall and Palmer, THIS JOURNAL, **61**, 927 (1939).

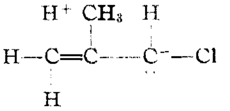
[28] Groves and Sugden, *J. Chem. Soc.*, 158 (1937).

[29] Hugill, Coop and Sutton, *Trans. Faraday Soc.*, **34**, 1518 (1938).



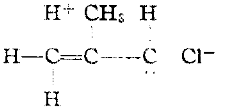
$$\mathrm{H{-}\overset{H}{C}^{-}{-}\overset{H}{C}{=}Cl^{+}}$$

Because of the similarity in behavior of the chlorides and cyanides, it appeared that replacement of an end hydrogen of vinyl chloride by a methyl group would provide indirect evidence as to the validity of the structure with positive nitrogen suggested as contributing to the structure of crotononitrile. The moment in Table II of isocrotyl chloride, in which both of the end hydrogens of vinyl chloride have been replaced by methyl groups, is again nearly 0.6 higher than that of vinyl chloride, indicating, as in the analogous cases of crotonaldehyde and crotononitrile, considerable contributions from structures such as



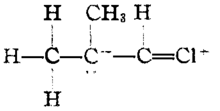
$$\mathrm{H{-}\underset{H}{\overset{H^{+}}{C}}{=}\overset{CH_3}{C}{-}\overset{H}{C}^{-}{-}Cl}$$

and



$$\mathrm{H{-}\underset{H}{\overset{H^{+}}{C}}{=}\overset{CH_3}{C}{-}\overset{H}{C}\quad Cl^{-}}$$

That, at the same time, the contribution from the structure



$$\mathrm{H{-}\underset{H}{\overset{H}{C}}{-}\overset{CH_3}{C}^{-}{-}\overset{H}{C}{=}Cl^{+}}$$

is reduced below that from the analogous structure in vinyl chloride is indicated by the fact that electron diffraction shows the shortening of the C—Cl bond by double bond character to be about half as great in isocrotyl chloride[30] as in vinyl chloride.[31] The parallelism observed between the effects for the chlorides and those for the cyanides provides evidence in support of the structures proposed for both.

The theory of hyperconjugation provides a mechanism for the explanation of pronounced differences in moment not readily explicable otherwise and thus receives experimental support from a new type of evidence.

Summary

The dielectric constants of the vapors of formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, crotonaldehyde, diketene, propionitrile, acrylonitrile, crotononitrile and isocrotyl chloride have been measured and used to calculate the dipole moments of the molecules.

The moment of the carbon-oxygen bond in the carbonyl group is recalculated and its inductive effect in aldehydes and ketones is examined.

Close analogies in behavior and in structure are found among unsaturated aldehydes, nitriles and chlorides. Resonance among structures made possible by the presence of a double bond may have a large effect upon the moment of a molecule. Hyperconjugation occurring when a hydrogen adjacent to a double bond is replaced by a methyl group produces a large increase in moment. The variations observed in the moment values are taken as qualitative evidence as to the relative stabilities of various polar structures which are proposed as contributing to the molecular structure.

PRINCETON, NEW JERSEY RECEIVED OCTOBER 3, 1942

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[30] Beach and Stevenson, THIS JOURNAL, 61, 2643 (1939).

[31] Brockway, Beach and Pauling, *ibid.*, 57, 2693 (1935).

[CONTRIBUTION FROM THE AMMONIA DEPARTMENT OF E. I. DU PONT DE NEMOURS AND COMPANY, INC.]

Optical Crystallographic Studies with the Polarizing Microscope. IV. Axial Dispersion with Change of Sign. Other Dispersion Measurements

BY W. M. D. BRYANT

The optical study of crystals under the microscope using monochromatic polarized light of different wave lengths has been found especially useful for the precise characterization of organic compounds. The various types of dispersion observed in interference figures are sensitive and distinctive optical properties, of frequent occurrence in the aromatic series and among certain classes of aliphatic compounds. The better known types of dispersion of the optic axes and ellipsoidal axes were exemplified and discussed in the third paper of this series.[1]

The experimental investigation of dispersion in crystals has been continued and in the present

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[1] Bryant, THIS JOURNAL, 63, 511 (1941). The term "selective dispersion," employed in paper III to describe the various types of dispersion of the optic axes and indicatrix axes, has been used earlier in quite a different sense, namely, as a synonym for *anomalous dispersion*, the term applied to simple dispersion in which the usual order of spectral deviation is altered by absorption. Since retention of the earlier usage is desirable, the name "ellipsoidal dispersion" should replace "selective dispersion" in paper III.