[A CONTRIBUTION FROM NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Electronic Properties of Alkyl Groups. II. The Dipole Moments of Alkyl Benzenes and Derivatives

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RECEIVED DECEMBER 3, 1958

The dipole moments of some *p*-alkylbenzene derivatives have been determined in cyclohexane, dioxane and chloroform solutions. Along with data on other series of *p*-alkyl derivatives taken from the literature the results are analyzed to determine the nature and magnitude of the contributions made by the alkyl groups to the over-all moments. In considering the data for non-polar solvents, it is found that when a correction is made to account for the electrostatically induced moment in the alkyl groups, the variation in moment in a series of *p*-alkyl compounds is approximately independent of the functional group located in the *para*-position. These results do not appear consistent with the idea that hyperconjugation plays an important role in affecting the electron-releasing ability of alkyl groups in this class of compounds. The dipole moment data for the *p*-alkylbenzonitriles in dioxane and chloroform are in the Baker–Nathan order after the correction for induced moment. This result is in agreement with the proposal that the solvent plays an important role in affecting the apparent relative electron-releasing abilities of alkyl groups.

The operation of hyperconjugative interactions in affecting the electric dipole moments of alkyl-containing compounds has been discussed in a number of places.[1–3] In general there does not appear to be any unambiguous evidence from these studies that hyperconjugation does contribute significantly to variations in dipole moment. Except for the alkylbenzenes, however, aromatic alkyl-containing compounds have not received much consideration in connection with this problem. In the present paper the moments of the *p*-alkylbenzonitriles and two nitrobenzene derivatives are reported and interpreted along with literature values for the moments of analogous series of aromatic compounds.

Experimental

Materials.—Cyclohexane was purified by passage through a 60 cm. column of acid-washed alumina, followed by careful fractional distillation from phosphorus pentoxide. Storage was over sodium wire, $d_{24} = 0.77410$.

Dioxane was dried with anhydrous magnesium sulfate, refluxed with sodium and then fractionally distilled. Storage was over sodium wire, $d_{24} = 1.0292$.

Chloroform was refluxed with phosphorus pentoxide and then simply distilled. Storage was under dry nitrogen gas in the dark, $d_{24} = 1.4754$.

p-Tolunitrile was Eastman White Label Material, dried with magnesium sulfate, fractionally crystallized once (m.p. 28°) and then fractionally distilled under reduced pressure in a six inch spinning band column. Center fractions of constant refractive index were collected for use.

p-Ethylbenzonitrile was prepared from *p*-ethylacetophenone by oxidation to the acid with sodium hypochlorite,[4] this in turn was converted to the acid chloride with thionyl chloride.[5] The acid chloride was converted to the amide, which when purified was treated with excess phosphorus oxychloride and sodium metabisulfite[6] added. The reaction mixture was poured carefully onto ice, and after completion of the hydrolysis the non-aqueous layer was separated and steam distilled. The nitrile collected in this way was dried with anhydrous magnesium sulfate and fractionated under reduced pressure as described above for the methyl compound.

The *p*-isopropyl and *p*-*t*-butyl compounds were prepared as just described for the ethyl compound, except that the acids were used as starting materials. Vapor phase chromatograms of each compound failed to reveal any impurity. In Table I are listed the refractive indices and the results of elemental analyses of the pure materials.

Benzonitrile was obtained commercially, dried and carefully fractionated; $n^{25}\text{D}$ 1.5261.

Nitrobenzene was fractionally crystallized, dried and then fractionated; $n^{25}\text{D}$ 1.5501.

p-Methylnitrobenzene was Eastman material, recrystallized from methanol six times and then dried. After initial drying the material was ground to a fine powder and dried in a vacuum desiccator; m.p. 52.0°.[7]

p-*t*-Butylnitrobenzene was fractionally crystallized from a mixture of the mononitro isomers. The fractional crystallization was repeated twice, followed by recrystallization from methanol twice and finally vacuum drying; m.p. 28.4°.[7]

Apparatus and Procedure.—The apparatus employed in the measurements of dielectric constant has been described.[8] The resonance frequency settings on the converted BC-221 frequency meter were calibrated with a General Radio 722-D precision capacitor. The dielectric constants of cyclohexane and chloroform at the bath temperature of 23.97° were taken as 2.017 and 4.744, respectively. The dielectric constant of dioxane was determined with reference to a sample of purified benzene[8] to be 2.227. At least four separately prepared solutions of each compound were employed in evaluating each dipole moment. Weight fractions were in the range 0.0007 to 0.008. It was not found possible to obtain refractive index measurements with enough precision to permit a reliable evaluation of the electronic polarizations, so the values calculated from bond refractions were employed. The values obtained experimentally from the dioxane solutions of the *p*-alkylbenzonitriles were most nearly acceptable and are reported for comparisons. Densities were obtained with a 5-ml. pycnometer with calibrated side-arms.

Results

From the experimental quantities, values of $\alpha = \partial\epsilon/\partial\omega_2$ and $\beta = \partial\nu/\partial\omega_2$, where ϵ is the dielectric constant, ν is the specific volume and ω_2 is weight fraction of solute, were obtained for each compound. The method of Halverstadt and Kumler[9] was employed for calculation of the molar polarization P_2, with the exception that the data on the pure solvent were weighted equally with the solutions. In Table II are listed the results for the *p*-alkylbenzonitriles in the three solvents, along with the values of R_2 obtained from the refractive index measurements on the dioxane solutions, listed as R_2 (obsd., cm.^{3}). Table III lists the results for the

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(1) J. W. Baker, "Hyperconjugation," Oxford Univ. Press, London, 1952, p. 25.

(2) J. W. Smith, "Electric Dipole Moments," Butterworths, London, 1955, chapter 7.

(3) C. P. Smyth, "Chemical Architecture," Interscience Publishers, Inc., New York, N. Y., 1948, p. 23.

(4) A. M. Van Arendonk and M. E. Cupery, THIS JOURNAL, **53**, 3184 (1931).

(5) W. J. Hickenbottom, "Reactions of Organic Compounds," 2nd Ed., Longmans, Green and Co., New York, N. Y., 1948, p. 226.

(6) M. J. Fahrenbach, U. S. Patent 2,459,128; *C. A.*, **43**, 3170*b* (1949).

(7) W. M. Schubert, J. Robins and J. L. Haun, THIS JOURNAL, **79**, 910 (1957).

(8) T. L. Brown, D. Y. Curtin and R. R. Fraser, *ibid.*, **80**, 4339 (1958).

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

TABLE I

REFRACTIVE INDICES AND RESULTS OF ELEMENTAL ANALYSES OF PURIFIED *p*-ALKYLBENZONITRILES

Benzonitriles	$n^{25}D$	Carbon, % Calcd.	Carbon, % Obsd.	Hydrogen, % Calcd.	Hydrogen, % Obsd.	Nitrogen, % Calcd.	Nitrogen, % Obsd.
p-Methyl	1.5269	81.98	82.27	6.02	5.78	11.95	11.72
p-Ethyl	1.5235	82.45	82.62	6.90	7.12	10.69	10.76
p-Isopropyl	1.5202	82.71	82.48	7.64	7.49	9.64	9.45
p-*t*-Butyl	1.5168	82.98	82.98	8.24	8.19	8.80	8.89

nitrobenzenes and for benzonitrile. Previously reported values, sometimes in another solvent, are listed for comparison.

TABLE II

VALUES OF DIPOLE MOMENT FOR *p*-ALKYLBENZONITRILES IN VARIOUS SOLVENTS AT 24°

Benzonitriles	*p*-Methyl	*p*-Ethyl	*p*-Isopropyl	*p*-*t*-Butyl
R_2 (calcd., cm.^{3})	34.1	38.8	43.5	48.3
R_2 (obsd., cm.^{3})	36.5	41.1	44.4	49.6
Cyclohexane				
α	14.38	13.50	12.60	10.90
β	−0.269	−0.257	−0.216	−0.212
P_2 (cm.^{3})	435	460	479	490
μ (Debye)	4.42	4.53	4.60	4.64
Dioxane				
α	23.0	20.9	19.2	17.8
β	0.040	0.040	0.038	0.045
P_2 (cm.^{3})	474	486	502	509.1
μ (Debye)	4.63	4.67	4.71	4.74
Chloroform				
α	25.6	23.3	21.7	19.0
β	0.337	0.350	0.374	0.380
P_2 (cm.^{3})	200	212	225	229
μ (Debye)	2.85	2.90	2.97	2.97

TABLE III

VALUES OF DIPOLE MOMENTS FOR NITROBENZENES AND FOR BENZONITRILE IN CYCLOHEXANE AT 24°

Compound	$C_6H_5NO_2$	*p*-CH_3-$C_6H_4NO_2$	*p*-*t*-C_4H_9-$C_6H_4NO_2$	C_6H_5CN
R_2 (calcd., cm.^{3})	32.9	37.5	51.6	29.5
α	11.1	12.4	10.3	13.5
β	−0.437	−0.400	−0.334	−0.259
P_2 (cm.^{3})	355	440	487	372
μ (Debye)	3.96	4.43	4.61	4.08
μ (lit.)	3.93[a]	4.42[b]	4.61[c]	4.10[d]

[a] Ref. *e*, Table IV, p. 29 (in C_6H_6). [b] Ref. *e*, Table IV, p. 35 (in C_6H_6). [c] C. G. LeFevre, R. J. W. LeFevre and K. W. Robertson, *J. Chem. Soc.*, 480 (1935) (in C_6H_6). [d] E. G. Cowley and J. R. Partington, *ibid.*, 1184 (1936).

Discussion

A. *para*-Alkyl Compounds in Non-polar Solvents.—In Table IV are listed the values of dipole moment for a number of *p*-alkyl compounds measured in non-polar solvents. Since all of these values are in non-polar solvents, the variations in moment in any one series should be comparable with that in another. At first sight these data would seem to show that in general the *t*-butyl group is more electron-releasing than methyl, and furthermore that it becomes even more electron-releasing relative to methyl when an electron-demanding group is located *para* to the alkyl. For example in the alkylbenzenes the difference in moments between the methyl and *t*-butyl compounds is 0.08 Debye, whereas in the nitrobenzene and benzonitrile series it is 0.18 and 0.22 Debye, respectively. Conclusions based on these results are most certainly not in accord with the idea that C–H hyperconjugative electron-release is of significance. In order to assess these results properly, however, certain corrections to be discussed below must be made. Nevertheless, after such corrections have been applied, it will be seen that the dipole moment results are *not* in accord with the hypothesis that on demand preferential electron-release *via* C–H hyperconjugation occurs to any appreciable extent.

TABLE IV

VALUES OF DIPOLE MOMENT AND CORRECTED DIPOLE MOMENT FOR SOME SUBSTITUTED ALKYLBENZENE SERIES

Compound	Solvent	μ(Debye)	μ	$\mu_{corr.}$	Ref.
Benzene	C_6H_6	0	..	0	..
Toluene	C_6H_6	.37	..	0.37	*a*
Ethylbenzene	C_6H_6	.39	..	.39	*a*
Isopropylbenzene	C_6H_6	.43	..	.43	*a*
t-Butylbenzene	C_6H_6	.45	..	.45	*a*
Phenylacetylene	C_6H_6	0.66 (0.73)	..	0.70	*b*
p-Methylphenylacetylene	C_6H_6	1.01	0.01	1.00	*c*
p-Ethylphenylacetylene	C_6H_6	1.05	.02	1.03	*c*
p-Isopropylphenylacetylene	C_6H_6	1.12	.03	1.09	*c*
Nitrobenzene	C_6H_{12}	3.96	..	3.96	*d*
p-Methylnitrobenzene	C_6H_{12}	4.43	.08	4.35	*d*
p-*t*-Butylnitrobenzene	C_6H_{12}	4.61	.26	4.35	*d*
Benzonitrile	C_6H_{12}	4.08	..	4.08	*d*
p-Methylbenzonitrile	C_6H_{12}	4.42	.06	4.36	*d*
p-Ethylbenzonitrile	C_6H_{12}	4.53	.11	4.42	*d*
p-Isopropylbenzonitrile	C_6H_{12}	4.60	.16	4.44	*d*
p-*t*-Butylbenzonitrile	C_6H_{12}	4.61	.20	4.41	*d*
Bromobenzene	C_6H_6	1.53	..	1.53	*e*
p-Methylbromobenzene	C_6H_6	1.94	−0.05	1.99	*f,g*
p-*t*-Butylbromobenzene	C_6H_6	1.92	−0.14	2.06	*h*

[a] A. P. Altshuller, *J. Phys. Chem.*, **58**, 392 (1954). [b] (i) C. J. Wilson and H. H. Wenzke, THIS JOURNAL, **56**, 2025 (1934). (ii) H. Lumbroso, *Compt. rend.*, **228**, 1425 (1949). [c] M. M. Otto and H. H. Wenzke, THIS JOURNAL, **56**, 1314 (1934). [d] Present work. [e] L. G. Wesson, "Tables of Electric Dipole Moments," Technology Press, M. I. T. Cambridge, Mass., 1948, p. 28. [f] L. Tiganik, *Z. physik. Chem.*, **B13**, 425 (1931). [g] G. C. Hampson, R. H. Farmer and L. E. Sutton, *Proc. Roy. Soc.* (*London*), **A143**, 147 (1933). [h] M. T. Rogers, THIS JOURNAL, **77**, 3681 (1955).

In evaluating the moment of a *p*-alkyl compound, some account must be taken of the moment which is induced in the alkyl group by the presence of a dipole in the remainder of the molecule. This induced moment could be evaluated accurately if the charge distribution in the molecule were known. In general only the total dipole moment resulting from this distribution is known. It is possible, however, in a somewhat artificial way, to separate the total dipole moment of a molecule, *e.g.*, nitrobenzene, into three components. These are the group moment (the moment of the nitro group), the induced moment (induced in the phenyl ring by the nitro group moment) and the mesomeric moment (the moment produced by resonance interaction of the nitro group with the ring). These components have been evaluated rather successfully by Groves and Sugden[10] for a number of substituted benzenes. The moment induced in the alkyl group is then calculated as the sum of the moments induced by each of these three components. The location of the moment induced in the ring by the functional group cannot be determined with any assurance, but it surely lies near the inducing group, since induction falls off rapidly with distance. In the interests of uniformity the group moment plus the induced moment will be considered as a single dipole at a distance of 5.1 Å. from the alkyl group.[11] The mesomeric moment is taken to be centered in the ring, so the distance to the alkyl group for this dipole is about 2.8 Å.[11]

The values of mesomeric moment for nitrobenzene, benzonitrile and bromobenzene are given by Groves and Sugden[10,12]; the differences between these and the observed moments then are taken as the group-plus-induced moment (the mesomeric moment for phenylacetylene is essentially zero). In this way the mesomeric and group-plus-induced dipoles, respectively, are for each compound: nitrobenzene, 0.25, 3.71; benzonitrile, 0.05, 4.03; bromobenzene −0.74, 2.27; phenylacetylene, 0.0, 0.73.

The moment induced in a polarizable group which lies on the axis of a dipole and at a distance *r* is given by

$$\mu_i = \frac{2\mu\alpha}{\epsilon r^3} \qquad (1)$$

where μ_i is the induced moment, μ is the inducing dipole, α is the polarizability of the group and ϵ is the dielectric constant of the intervening medium, here taken as 2.5. The polarizabilities of the methyl, ethyl, isopropyl and *t*-butyl groups attached to the phenyl ring have been evaluated.[13] Applying equation 1 to each of the compounds in Table IV (except the alkylbenzenes) and summing the dipoles induced in the alkyl group by each of the two moments given above, the values of μ_i listed for each compound in Table IV were obtained. (It is interesting to note that the direction of the induced dipole is opposite in direction to the over-all moment in the bromobenzenes. Such a result appears quite reasonable when it is recognized that the induced moment is determined by the particular charge distribution in the parent molecule, as approximated by superposing the two dipoles given above, rather than by a single dipole located at any one point). In addition to the induced dipole of electrostatic origin, other factors contribute to a change in dipole moment upon substituting an alkyl group for hydrogen. The C–C bond joining the alkyl group to the ring is polarized in the sense $C_{alkyl} \rightarrow C_{ring}$ because of the greater electronegativity of the ring carbon arising from its sp^2 hybridization. The polarization in this bond is augmented to some extent by induced polarization in the adjacent C–C and C–H bonds of the alkyl. Since the C–C bonds are more polarizable than C–H along the bond axis, it is to be expected that substitution of methyl for hydrogen on the central alkyl carbon will result in a slight increase in moment. Petro has recently attempted an analysis of some observed electric moment results which includes some of the factors mentioned above.[14] There is some uncertainty, however, as to whether the C–H bond moments determined from infrared absorption studies which he employs actually correspond to static bond moments.[15]

The inductive effect, operating along the skeletal structure, of the group *para* to the alkyl, is probably not felt to a significant extent at the alkyl group. Some evidence that this is the case is found in Table IV. In the fifth column, the values of μ_{cor} represent the moments of the compounds after the electrostatically induced moment has been corrected for. In comparing the moments of the unsubstituted derivative with the corresponding *p*-methyl compounds, it is seen that there is an increase in moment in each case; the average value is 0.37 ± 0.06 *D*. There is no apparent regular increase in this increment as the group *para* to the alkyl becomes more electronegative. However, even if a small moment were being induced by this means in the C–C bond joining the alkyl group to the ring it would not, if this moment were of the order of 0.05–0.10 *D*., produce any marked effect on the *relative* values of moment among the various alkyl groups, since the bond is common to all of them. The only effect which could result from such a small additional C–C moment would arise as a result of the difference in polarizabilities of the C–C and C–H bonds in the alkyl groups and would be quite small. This conclusion regarding the inductive effect is not inconsistent with reactivity and other structural considerations. Much of what passes for inductive effect in the literature is actually the result of the electrostatic contributions which already have been accounted for in the system under discussion.

In view of the above considerations, subtraction of the electrostatically induced moment μ_i from the total moment should reveal variations in moment due to simple polarization of C_{alkyl}–C_{ring}, and induced polarization of adjacent C–H or C–C, bonds. Of course, this assumes that hyperconjugation is not operative.

It can be seen from Table IV, that a regularity in μ_{cor} exists in all of the series of compounds. The increment in moment between each of the alkyl derivatives in each series is the same within experimental error, with the exception of the nitrobenzenes.[16]

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[10] L. G. Groves and S. Sugden, *J. Chem. Soc.*, 1992 (1937).

[11] The center of the alkyl group is taken as the location of the central alkyl carbon atom. The sum of the moment induced in the ring and the functional group moment should lie nearer the alkyl group than the functional group moment alone. The point which is 5.1 Å. from the alkyl group lies about 0.8 Å. beyond the opposite side of the ring, the point which is 2.8 Å. away lies in about the center of the ring.

[12] The mesomeric moment for nitrobenzene is given here as 0.25 *D*, in conformance with recent estimates of the best value of the vapor phase moment of nitrobenzene, ref. 2, p. 86.

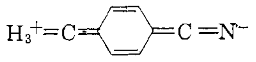
[13] T. L. Brown, THIS JOURNAL, **81**, 3229 (1959).

[14] A. J. Petro, *ibid.*, **80**, 4230 (1958).

[15] T. L. Brown, *Chem. Revs.*, **58**, 581 (1958).

[16] The relative values of dipole moment are probably accurate to about 0.03 *D*., the difference between the *p*-methyl and *p*-*t*-butylnitro compounds is zero whereas in the other series it is about 0.08 *D*., so that the discrepancy, though small, is outside experimental error. It may arise from the crudity of the model, *e.g.*, the location of the group-plus-induced dipole, or in the value assigned to the mesomeric moment in nitrobenzene.

This constancy, independent of the electron-attracting properties of the group which is *para* to the alkyl, is just what one would expect if only the contributions to the moment discussed above were operative. The result does not appear consistent with the idea that hyperconjugation makes an important contribution. If hyperconjugation were operative in these systems its importance would increase in, for example, the benzonitriles as compared with the alkylbenzenes because of the contribution from the resonance structure



If it is granted that C–H hyperconjugation is more important than C–C, then the spread in corrected moments should decrease in the benzonitriles and nitrobenzenes (and to a lesser extent in the phenylacetylenes), as compared with the alkylbenzenes. This is not observed to be the case, except in the nitrobenzenes where a small decrease is noted.

The increase in corrected moment upon substitution of methyl for the ring hydrogen in each series can be ascribed to the polarization of the C_{alkyl}–C_{ring} bond and adjacent C–H bonds, as discussed above. The subsequent small increase on substitution of methyl for hydrogen in the alkyl group is assigned to the greater induced moments in the C–C bonds as compared with the C–H.

Finally, the encouraging fact should be noted that the corrected moments for the bromobenzenes are relatively the same as for the other series, although the correction in these compounds is of opposite sign.

These results do not by any means rule out the possibility that hyperconjugative interactions between the alkyl group and the ring exist, but they do place some limit on their importance in affecting the electron distribution in the molecule. In addition they serve to emphasize the importance of considering the polarizabilities of alkyl groups in discussing their effect on molecular properties.

B. The Effect of Solvent.—Schubert and coworkers have advanced the hypothesis that steric inhibition of solvation is important in determining the apparent order of electron release by alkyl groups in systems where an electron-demand is measured.[7,17] In order to test the effect of solvent on the dipole moments, the *p*-alkylbenzonitriles were studied in dioxane and chloroform solutions. From the data in Table II it is clear that the spread in moments is significantly smaller in dioxane than in cyclohexane. Dioxane, although essentially non-polar, is nevertheless basic in character and is presumably capable of solvating electron-deficient sites in the solute molecules. If the corrections for induced moments are applied to these results a Baker–Nathan order will result.

The dipole moments calculated from the measurements on chloroform solutions have no particular significance as regards their absolute magnitude; it is well recognized that correct values of dipole moment cannot be determined by measurements in polar solvents.[18] Nevertheless for a series of molecules of similar dipole moment and molecular shape the effect of the polar solvent should be the same on all of the compounds in the series, so that the relative values may have significance. Whether this is true or not, it can simply be noted that the spread in apparent moments is again smaller than in the cyclohexane solutions.

Acknowledgments.—This work was sponsored in part by The Office of Naval Research. The author wishes to thank Dr. K. L. Rinehart for reading and criticizing the manuscript.

(17) (a) W. M. Schubert and A. Sweeney, THIS JOURNAL, **76**, 4625 (1954); (b) *J. Org. Chem.*, **21**, 119 (1956).

(18) Ref. 2, p. 164.

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[CONTRIBUTION FROM THE ESSO RESEARCH AND ENGINEERING COMPANY]

Stereospecific Isomerization of Butene-1 to Butene-2 over SiO_2–Al_2O_3 Catalyst

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RECEIVED NOVEMBER 5, 1958

The double bond isomerization of butene-1 to *cis*- and *trans*-butene-2 has been studied over silica–alumina catalyst. With either neutron irradiated or ordinary catalyst, the isomerization was observed to be stereospecific. The thermodynamically unfavored *cis*-butene-2 is kinetically favored and the *cis*/*trans* ratio is decidedly in favor of the *cis*-form, especially at low conversions. This result cannot be reconciled with conventional carbonium ion theory.

Introduction

Recent work in this Laboratory has been concerned with the effect of neutron pre-irradiation on the activity of silica–alumina catalysts for the isomerization of butene-1 to *cis*- and *trans*-butene-2. The results of this work, which are reported in a separate paper, showed that neutron pre-irradiation decreased the catalytic activity of silica–alumina. Only the catalytic activity of the catalyst was affected by radiation, since it was found that at a given degree of conversion the product distribution was the same for irradiated and ordinary catalysts, the product consisting almost entirely of *cis*- and *trans*-butene-2. Of greater interest than the observed effect of neutron irradiation was the finding that the isomerization is markedly stereospecific, since the thermodynamically unfavored *cis*-isomer is kinetically favored, especially at low conversions. The stereospecific nature of this reaction is discussed in the present paper.

Experimental

Catalysts and Reagents.—The catalyst used in this work was Davison SiO_2–Al_2O_3 (13 wt. % alumina) pressed into