

Dipole Moments of Some *para*-Substituted Phenylcyclopropanes

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Abstract: Dipole moments of phenylcyclopropane and *p*-methoxy-, *p*-chloro-, *p*-bromo-, *p*-nitro-, *o*-nitro-, and *p*-carboxyphenylcyclopropane have been determined in benzene or dioxane. The additivity relationship of the group dipoles is clearly demonstrated in all compounds on the assumption that the cyclopropyl group is positive relative to the benzene ring. The cyclopropyl group in these derivatives releases electron density to the benzene ring. In benzene, *p*-cyclopropylbenzoic acid exhibits a lower moment than expected, but this was the only exception in the additivity treatment; in dioxane, it showed the moment for a monomeric form, and two group dipoles were clearly shown to be additive.

To help clarify the characteristic electronic structure of a cyclopropane,¹ it is of interest to investigate its chemical behavior in interaction with another function, such as a methoxy or a nitro group. In the present study, attention is focused on the static behavior of a cyclopropyl group interacting with a variety of groups.

Some years ago, Roberts and his co-workers studied the dipole moments of cyclopropyl chloride² and bromide³ and noted appreciably lower moments than those of ordinary alkyl halides. They concluded that the cyclopropyl group withdraws electron density, which is consistent with acidic and basic strengths of cyclopropylcarboxylic acid and cyclopropylamine.³

On the other hand, Mazheiko, Giller, Gembitskii, and Levina⁴ have reported the dipole moments of some substituted phenylcyclopropanes, where the cyclopropyl group is conjugated with a benzene ring, and conclude that the cyclopropyl group releases electron density to the benzene ring. This argument holds for *p*-bromophenylcyclopropane and two other alkyl-substituted bromophenylcyclopropanes studied by them, but attention should be called to the inconsistency found for *p*-cyclopropylbenzoic acid, whose moment (1.16 D.) is remarkably lower than that of benzoic acid (1.64 D.).⁴ The cyclopropyl group in this molecule withdraws electron density from the benzene ring,⁵ contradictory to their conclusion.

Thus in some cases a cyclopropyl group withdraws electron density, while in others it releases it, and it is hardly predictable how the cyclopropyl group may behave when it interacts with a variety of functions. Consequently, it is highly desirable to study the static behavior of a cyclopropyl group under conditions where its effect can be evaluated with fewest complications. The present paper aims at an extensive investigation of the dipole moments of substituted phenylcyclopropanes; in the study of dipole moments of benzene derivatives, the electronic effect of the substituent is known to be

reflected on the group dipole, and the additivity relationship of group dipoles has been well developed.⁶

Results

Materials. Phenylcyclopropane, *p*-chloro-, and *p*-bromophenylcyclopropane were prepared from the corresponding styrene derivatives *via* the Simmons-Smith reaction.⁷ *p*-Bromophenylcyclopropane was converted to the Grignard reagent and the latter treated with carbon dioxide to afford *p*-cyclopropylbenzoic acid.⁸ Phenylcyclopropane was nitrated at a low temperature,⁹ and the resulting *p*-nitro and *o*-nitro derivatives were separated by means of a preparative vpc. All materials used for the measurements of the electric moment showed satisfactory elemental analyses, and their structures were ascertained by means of infrared, ultraviolet, and nmr spectra.

Apparatus and Method. Electric moments were determined in benzene or dioxane at 25.0, 35.0, or 45.0°. The dielectric constants were measured at 1.5 Mc with a heterodyne beat apparatus.¹⁰ Determinations of the dielectric constant and density of the solution were made on a series of four or five solutions of different concentrations; the resulting dielectric constant (ϵ_{12}) and specific volume (v_{12}) of the solutions were plotted graphically against the weight fractions of the solute, and the intercepts at zero weight fraction (ϵ_1 and v_1) were used in the calculation.¹¹ The electric polarizations were obtained from bond refraction values given by Vogel¹² and Smyth.¹³ The details of the measurements and calculations are given in the Experimental Section. The dipole moments (with standard errors) and related data are summarized in Tables I and II. The accuracy of the experimental procedures was checked by comparison with known compounds, such as chlorobenzene, anisole, and nitrobenzene; all of the observed values were in excellent agreement.¹⁴

(1) (a) C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.*, **15**, 151 (1947); *Phil. Mag.*, **40**, 1 (1949); (b) J. M. Sugden, *Nature*, **160**, 367 (1947); (c) A. D. Walsh, *ibid.*, **159**, 165, 712 (1947); *Trans. Faraday Soc.*, **45**, 179 (1949).

(2) M. T. Rogers and J. D. Roberts, *J. Am. Chem. Soc.*, **68**, 843 (1946).

(3) J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 5030 (1951).

(4) I. B. Mazheiko, S. S. Giller, P. A. Gembitskii, and R. Ya. Levina, *Zh. Obshch. Khim.*, **33**, 1698 (1963).

(5) In the calculation of the dipole moment of *p*-cyclopropylbenzoic acid, they assume an opposite direction for the cyclopropyl group to that considered in other cases and show an agreement between the observed and the calculated moment.⁴

(6) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., Inc., New York, N. Y., 1955.

(7) H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

(8) A. S. Hussey, *ibid.*, **73**, 1364 (1951).

(9) R. Ketcham, R. Cavestri, and D. Jambotkar, *J. Org. Chem.*, **28**, 2139 (1963).

(10) J. Y. Chien, *J. Chem. Educ.*, **24**, 494 (1947).

(11) I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).

(12) A. I. Vogel, *J. Chem. Soc.*, 514 (1952).

(13) Reference 6, p 409.

(14) Reference 6, p 314.

Table I. Summary of Dipole Moments and Related Data in Benzene at 25.0°

Phenyl-cyclopropane	ϵ_1^a	α^b	v_1^c	β^d	P_{20}^e	PE_2^f	$\mu, D.^g$
Hydrogen	2.2726	0.275	1.1450	-0.0783	43.67	38.95	0.48 ± 0.04 ^h
<i>p</i> -OCH ₃	2.2735	1.0483	1.1452	-0.1361	73.78	44.99	1.19 ± 0.03
<i>p</i> -Cl	2.2727	3.1060	1.1449	-0.2258	130.98	43.07	2.07 ± 0.01
<i>p</i> -Br	2.2729	2.3878	1.1448	-0.4238	130.85	46.96	2.03 ± 0.01 ⁱ
<i>p</i> -NO ₂	2.2736	14.385	1.1450	-0.4048	477.53	43.94	4.61 ± 0.02
<i>o</i> -NO ₂	2.2718	9.0485	1.1460	-0.4958	309.78	43.94	3.61 ± 0.04
<i>p</i> -COOH	2.2722	1.3408	1.1448	-0.2817	82.61	44.80	1.36 ± 0.10 ^j

^a Dielectric constant extrapolated to zero concentration, obtained by the least-squares treatment. ^b Slope of ϵ_{12} vs. w_2 plot. ^c Specific volume extrapolated to zero concentration, obtained by the least-squares method. ^d Slope of v_{12} vs. w_2 plot. ^e Molecular polarization. ^f Electronic polarization obtained from atomic refractions. ^g Dipole moment with the standard error. ^h Reported values are 0.51 D.¹ and 0.49 D.⁴ ⁱ Lit.⁴ 2.02 D. ^j Lit.⁴ 1.16 D.

Table II. Dipole Moments of *p*-Cyclopropylbenzoic Acid in Dioxane^a

Temp, °C	ϵ_1	α	v_1	β	P_{20}	PE_2	$\mu, D.$
25.0	2.2080	3.3306	0.97284	-0.12337	128.59	44.80	2.03 ± 0.04
35.0	2.1920	3.4302	0.98356	-0.19061	129.99	44.80	2.08 ± 0.04
45.0	2.1752	3.4580	0.99469	-0.14020	130.45	44.80	2.11 ± 0.05

^a Symbols given are the same as those used in Table I.

Table III. Comparison between Observed and Calculated Values of Dipole Moment

Phenyl-cyclopropane	Solvent	Temp, °C	$\mu_{\text{obsd}}, D.$	$\mu_{\text{calcd}}, D.^a$
<i>p</i> -OCH ₃	Benzene	25.0	1.19	1.22 ^b
<i>p</i> -Cl	Benzene	25.0	2.07	2.06
<i>p</i> -Br	Benzene	25.0	2.03	2.02
<i>p</i> -NO ₂	Benzene	25.0	4.61	4.46
<i>o</i> -NO ₂	Benzene	25.0	3.61	3.73
<i>p</i> -COOH	Benzene	25.0	1.36	1.83 ^c
	Dioxane	...	2.07 ^d	1.97 ^c

^a The following moments¹⁴ are used in the calculations: phenyl-cyclopropane, 0.48 D. (see Table I); anisol, 1.25 D.; chlorobenzene, 1.58 D.; bromobenzene, 1.54 D.; nitrobenzene, 3.98 D.; benzoic acid, 1.64 D. (in benzene) and 1.78 D. (in dioxane).¹⁶

^b Calculated by taking the moment angle is 105°. ¹⁵ ^c The moment angle: 74°; ¹⁶ the moment for the cyclopropyl group in dioxane is assumed to be the same as that given in benzene. ^d Mean value of the three measurements given in Table II.

The observed moments are compared with calculated ones in Table III; in the case of *p*-methoxy and *p*-carboxyl derivatives, the calculations are made with the moment angle of 105° for a methoxy group¹⁵ and 74° for carboxyl.¹⁶

Discussion

The electric dipole moment of phenylcyclopropane was determined first by Rogers in 1947,¹⁷ although the direction of the dipole has not been established. His value was confirmed by Russian workers⁴ and by the present experiment; thus the value 0.48 D. is taken for the group dipole of a cyclopropyl group in the following discussions. Because of the nonsymmetric structure, the cyclopropyl group should have a moment angle similar to those considered in methoxy¹⁵ and carboxyl;¹⁶ but the absolute value of the moment is very small and,

(15) G. Klages and E. Klopping, *Z. Elektrochem.*, **57**, 369 (1953).

(16) C. S. Brooks and M. E. Hobbs, *J. Am. Chem. Soc.*, **65**, 967 (1943).

(17) M. T. Rogers, *ibid.*, **69**, 2544 (1947).

therefore, the moment angle can be neglected. Consequently, the axis of the dipole of a cyclopropyl group is taken to be on the line connecting cyclopropane and the benzene ring.

***p*-Chloro- and *p*-Bromophenylcyclopropane.** *p*-Chloro- and *p*-bromophenylcyclopropane have higher moments than those of chlorobenzene and bromobenzene; a value obtained for *p*-bromo derivative is in a good agreement with that reported.⁴ Increments between halobenzene and *p*-halophenylcyclopropane, 0.49 D. in both halides, are exactly the moment given for the cyclopropyl group; namely, an exact additivity is established if the direction is so taken that cyclopropane is at the positive end of the dipole. Thus the cyclopropyl group in these compounds releases electron density to the benzene ring as stated by Russian workers.⁴ This observation is in marked contrast to those observed in cyclopropyl chloride and bromide by Roberts and his co-workers;^{2,3} in these halides, the cyclopropyl group withdraws electron density and makes their moments appreciably smaller than those of ordinary alkyl halides. The electron-withdrawing inductive effect of a cyclopropyl group is also demonstrated in the slightly more acidic character of cyclopropylcarboxylic acid^{3,18} and the basicity of cyclopropylamine.³ In Roberts' system, halogen and cyclopropane are joined directly, whereas in the present system, there exists a benzene ring between two groups. It is probable, therefore, that the electronic interaction of a cyclopropyl group with the adjacent unsaturated system¹⁹⁻²⁶ overcomes its electron-withdrawing induc-

(18) A. Albert and E. P. Serjeant, "Ionization Constants of Acids and Bases," Methuen and Co. Ltd., London, 1962, p 124.

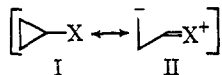
(19) For leading references see (a) M. Y. Lukina, *Russ. Chem. Rev.*, **31**, 419 (1962); (b) P. J. C. Fierens and J. Nasielski, *Bull. Soc. Chim. Belges*, **71**, 187 (1962); (c) M. Charton, *J. Chem. Soc.*, 1205 (1964); (d) A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).

(20) L. A. Strait, R. Ketcham, D. Jambotkar, and V. P. Shah, *ibid.*, **86**, 4628 (1964).

(21) (a) L. S. Bartell and J. P. Guillory, *J. Chem. Phys.*, **43**, 647 (1965); (b) L. S. Bartell, J. P. Guillory, and A. T. Parks, *J. Phys. Chem.*, **69**, 3043 (1965).

tive effect and that the net effect of the cyclopropyl group is electron releasing.

Roberts and his co-workers^{2,3} have proposed a small contribution of the polar structure II to the resonance hybrid in the cyclopropyl halides in order to account for their appreciably low moments; a similar contribution is considered in vinyl chloride.²⁷ If the same contribution is important in the present system, the same anomaly should be observed in *p*-halophenylcyclopropanes; moreover, a wide separation of the



positive and negative ends in the present case ought to bring about a larger effect of moment lowering than those observed in cyclopropyl halides. However, as mentioned above, the dipoles of the two groups are clearly additive; hence, such a contribution of the polar structure is of little significance in the present system. This conclusion is substantiated also in the case of *p*-methoxyphenylcyclopropane.

***p*-Methoxyphenylcyclopropane.** Because a *p*-methoxy group can stabilize an electron-deficient center much more effectively than a *p*-halo group,²⁸ the contribution of a polar structure (similar to II) to a resonance hybrid can be anticipated here more than in the case of *p*-halo derivatives, even though no contribution is noticeable in the latter case. The dipole moment found for *p*-methoxyphenylcyclopropane is 1.19 D., which is lower than that of anisole itself, 1.25 D.¹⁴ However, it is known that the direction of the dipole in anisole lies close to a line from methyl to oxygen and the moment angle is reported to be 105°. Based on this model, the dipole moment for *p*-methoxyphenylcyclopropane is calculated to be 1.22 D. by assuming that the cyclopropyl group releases electron density. Thus it is clear that the additivity relationship exists also in the *p*-methoxy derivative; the *p*-methoxy group is also incapable of interacting with the cyclopropyl group in spite of its much higher ability than a halogen to release the electron to an electron-deficient center.²⁸

The validity of these arguments is obvious when the dipole moments of *p*-halo- and *p*-methoxyphenylcyclopropane are compared with those of similarly substituted toluene and styrene derivatives (Table IV). The dipole moments of cyclopropyl halides are higher than those of vinyl halides, but lower than those of alkyl halides;^{2,3} on the other hand, *p*-chloro-, *p*-bromo-, and *p*-methoxyphenylcyclopropane have similar values to those of toluene derivatives, whereas styrene derivatives have much lower moments than those of saturated analogs. Thus, it is concluded that the cyclopropyl group does not act like an olefinic group but behaves

Table IV. Dipole Moments of *para*-Substituted Toluene, Phenylcyclopropane, and Styrene

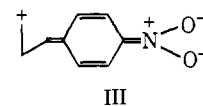
Compound	μ , D.		
	-CH ₃	R	-CH=CH ₂
<i>p</i> -ClC ₆ H ₄ R	1.94 ^a	2.07	1.50 ^b
<i>p</i> -BrC ₆ H ₄ R	1.96 ^a	2.03	1.52 ^b
<i>p</i> -CH ₃ OC ₆ H ₄ R	1.20 ^a	1.19	...

^a Reference 6, p 321. ^b K. B. Everard, L. Kumar, and L. E. Sutton, *J. Chem. Soc.*, 2807 (1951).

as an alkyl group in these phenylcyclopropane derivatives.

***p*-Nitro- and *o*-Nitrophenylcyclopropane.** As is well known, a cyclopropyl group greatly stabilizes an adjacent electron-deficient center, and this is most strikingly demonstrated in the cyclopropylcarbinyl system.²⁹⁻³⁷ Thus it would be of great interest to investigate the dipole moment of phenylcyclopropane substituted by a strongly electron-withdrawing group at the *para* position, and the dipole moments of *p*-nitro- and *o*-nitrophenylcyclopropane were accordingly investigated.

The observed and the calculated moments for *p*-nitro and *o*-nitrophenylcyclopropane show fair agreement (Table III). *p*-Nitrophenylcyclopropane gives a value only 0.15 D. higher than the calculated moment, and this deviation exceeds the value attributable to the experimental uncertainty. The *o*-nitro derivative exhibits a similar small deviation, which is in an opposite direction to that observed in the *para* derivative; the observed moment is lower than calculated by 0.12 D. These deviations from calculated values might be explained by contributions of the polar structure II



to the resonance hybrid as in the case of *p*-nitroaniline³⁸ and its derivative.³⁹ However, when these deviations are compared with those observed in toluene derivatives, it becomes apparent that their magnitudes are the same in the toluenes and phenylcyclopropanes (Table V). Consequently, it can be concluded that no more extraordinary electron-releasing character is present in the cyclopropyl group than that is demonstrated in a methyl group; a cyclopropyl group behaves like an alkyl group and not like one of the unsaturated groups as far as the dipole moment is concerned.

(29) J. D. Roberts and R. H. Mazur, *ibid.*, 73, 2509, 3542 (1951).

(30) C. G. Bergstrom and S. Siegel, *ibid.*, 74, 145 (1952).

(31) (a) H. Hart and J. M. Sandri, *ibid.*, 81, 320 (1959); (b) H. Hart and P. A. Law, *ibid.*, 84, 2462 (1962).

(32) (a) N. C. Deno, H. G. Richey, Jr., J. S. Liu, J. D. Hodge, J. J. Houser, and M. J. Wisotsky, *ibid.*, 84, 2016 (1962); (b) N. C. Deno, J. S. Liu, J. O. Turner, D. N. Lincoln, and R. E. Fruit, Jr., *ibid.*, 87, 3000 (1965); (c) N. C. Deno, H. G. Richey, Jr., J. S. Liu, D. N. Lincoln, and J. O. Turner, *ibid.*, 87, 4533 (1965).

(33) C. U. Pittman, Jr., and G. A. Olah, *ibid.*, 87, 2998, 5123 (1965).

(34) T. Sharpe and J. C. Martin, *ibid.*, 88, 1815 (1966).

(35) H. C. Brown and J. D. Cleveland, *ibid.*, 88, 2051 (1966).

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(37) T. Tsuji, I. Moritani, S. Nishida, and G. Tadokoro, *Tetrahedron Letters*, 1207 (1967).

(38) J. W. Smith and S. M. Walshaw, *J. Chem. Soc.*, 3217 (1957).

(39) J. B. Marsden and L. E. Sutton, *ibid.*, 599 (1936).

(22) G. L. Closs and H. B. Klinger, *J. Am. Chem. Soc.*, 87, 3265 (1965).

(23) H. Gunther and D. Wendish, *Angew. Chem. Intern. Ed. Engl.*, 5, 251 (1966).

(24) W. Lüttke and A. de Meijere, *ibid.*, 5, 512 (1966).

(25) G. R. DeMare and J. S. Martin, *J. Am. Chem. Soc.*, 88, 5033 (1966).

(26) S. W. Staley, *ibid.*, 89, 1532 (1967).

(27) J. A. C. Hugill, I. E. Coop, and L. E. Sutton, *Trans. Faraday Soc.*, 34, 1518 (1938).

(28) For example, $\sigma_p^+ - \sigma_p$ is -0.510 for methoxy and -0.113 for chloro; see L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, 1, 35 (1963), and H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, 80, 4979 (1958).

Table V. Dipole Moments of *p*-Nitro- and *o*-Nitro Derivatives

Compound	μ , D.		
	Obsd	Calcd	Dev ^a
<i>p</i> -Nitrophenylcyclopropane	4.61	4.46	0.15
<i>p</i> -Nitrotoluene ^b	4.45	4.35	0.10
<i>o</i> -Nitrophenylcyclopropane	3.61	3.73	-0.12
<i>o</i> -Nitrotoluene ^c	3.70	3.81	-0.11

^a $\mu_{\text{obsd}} - \mu_{\text{calcd}}$. ^b Reference 6, p 321. ^c Reference 6, p 332.

***p*-Cyclopropylbenzoic Acid.** The dipole moment of *p*-cyclopropylbenzoic acid has been studied by Russian workers,⁴ and a value 1.16 D. is given in benzene at 25.0°. This value is markedly lower than benzoic acid itself (1.64 D.) or the calculated value 1.83 D. (Table III); therefore, the additivity does not seem to hold for this compound. The Russian workers have reported a calculated value of 1.13 D. in which the cyclopropyl group had a dipole of an opposite direction to that concluded in other derivatives, in good agreement with their observed moment.

In the present investigation, the same compound was examined under similar conditions (*i.e.*, in benzene at 25.0°), giving a value of 1.36 D. in disagreement with the value given by Russian workers.⁴ Presumably, the reason for the discrepancy and for the observed moments being much lower than the calculated ones is that carboxylic acid derivatives are known to form polymeric species in nonpolar solvents such as benzene, and show a lower moment than that of a monomeric acid.⁴⁰ Consequently, in order to obtain a reliable value for the monomeric acid, the measurement must be carried out at a very low concentration or in a more polar solvent, such as dioxane.⁴⁰ Moreover, it is desirable to perform the measurements at different temperatures, because the dipole moment is independent of temperature while the degree of aggregation is not.⁴¹ Consequently, the dipole moment of *p*-cyclopropylbenzoic acid has been examined in dioxane at 25.0, 35.0, and 45.0°; the results are given in Table II. In benzene, the acid gave a value of 1.36 D. while in dioxane, it gave a value 2.03 D. at 25.0°, 2.08 D. at 35.0°, and 2.11 D. at 45.0°; three values coincided within the experimental error. The constancy in the moment observed at different temperatures and at very low concentrations (the measurements were performed at the weight fractions $1 \times 10^{-3} \sim 5 \times 10^{-3}$, at which a monomeric moment was obtained by others^{42,43}) clearly indicates that the value obtained in dioxane (2.07 D.) is the correct one for monomeric *p*-cyclopropylbenzoic acid. When this value is compared with the calculated one (1.97 D.), the additivity of two group dipoles is evident. It is concluded, therefore, that the cyclopropyl group in this acid also releases electron density to the benzene ring, and no resonance interaction between cyclopropane and carboxyl group at the *para* position is detected in the dipole moment.

(40) (a) H. A. Pohl, M. E. Hobbs, and P. M. Gross, *J. Chem. Phys.*, **9**, 408 (1941); (b) A. A. Maryott, M. E. Hobbs, and P. M. Gross, *ibid.*, **9**, 415 (1941).

(41) (a) R. S. Phadke, *J. Indian Inst. Sci.*, **35**, 123 (1953); (b) N. N. Stepaneko, B. A. Agranat, and V. F. Yakovlev, *J. Phys. Chem. USSR*, **21**, 893 (1947).

(42) C. J. Wilson and H. H. Wenzke, *J. Chem. Phys.*, **2**, 546 (1934).

(43) C. S. Brooks and M. E. Hobbs, *J. Am. Chem. Soc.*, **62**, 285 (1940).

Another possible feature which might operate in cyclopropylbenzoic acid is a protonation of the cyclopropane ring by a proton from the acid function, but the clear additivity observed in the acid excludes such a possibility.

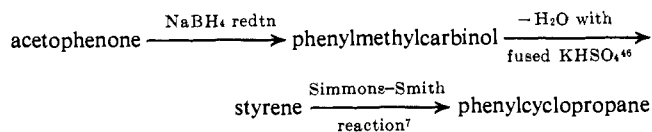
Conclusion

It is clearly established that the cyclopropyl group in substituted benzene derivatives is electron releasing. It is probable that the electronic interaction of a cyclopropyl with an olefinic group overcomes the electron-withdrawing inductive effect of the cyclopropyl and, therefore, the net effect of the cyclopropyl group is electron releasing. An interesting conclusion can be drawn from the relative magnitude of the electron-donating ability of the cyclopropyl group to those of other alkyls. Because of the exceedingly low moments observed for phenylcyclopropane and alkylbenzenes, the experimental uncertainty does not permit the direct evaluation of the relative magnitude from their dipole moments; but when the subtractions are made in the *p*-chloro derivatives, in which the additivities of group dipoles have been rigorously established,⁶ the value given for a cyclopropyl (0.49 D.) exceeds one for a methyl (0.36 D.). Evidently, the cyclopropyl group is more electron releasing than the methyl group.

Similar electron release by a cyclopropyl group has been observed in the hydroboration of vinylcyclopropane and a related olefin.⁴⁴ The present results not only confirm the former observations but also show that the electron-releasing character of the cyclopropyl is apparent even under a static situation. Finally, the exact additivities observed in all derivatives examined here evidently indicate that no extraordinary resonating ability is noticeable for the cyclopropyl group either when it interacts with a strongly electron-releasing *p*-methoxy or a strongly electron-withdrawing *p*-nitro group. Thus, as far as the dipole moments are concerned, the cyclopropyl group is properly considered to be like an alkyl group.

Experimental Section

Materials.⁴⁶ *p*-Methoxy, *p*-chloro-, and *p*-bromophenylcyclopropane were prepared according to the following sequence.



Physical constants of substituted styrenes and phenylcyclopropanes are given in Table VI. The final stage of the synthesis (*i.e.*, the addition of methylene iodide—zinc—copper couple to styrene derivatives) was accompanied by extensive polymerization, especially in the case of the *p*-methoxy derivative; the yield of *p*-methoxyphenylcyclopropane was only 2%, but preparation on a large scale gave a satisfactory amount for purification and the investigation of its electric moment.

(44) S. Nishida, I. Moritani, K. Ito, and K. Sakai, *J. Org. Chem.*, **32**, 939 (1967).

(45) Boiling points and melting points are uncorrected. Infrared spectra were recorded by a Hitachi EPI-S2 infrared spectrophotometer; ultraviolet spectra were obtained by a Hitachi EPS-2U spectrophotometer; nmr spectra were recorded by a Japan Electron Optics JNM-4H-100 spectrometer. Microanalyses were performed by the Micro-analytical Laboratory, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan.

(46) C. S. Marvel and G. L. Schertz, *J. Am. Chem. Soc.*, **65**, 2054 (1943).

Table VI. Physical Constants of Styrenes and Phenylcyclopropanes

Compound	Yield, %	Bp, °C (mm)		n_D^{20}	
		Obsd	Lit.	Obsd	Lit.
<i>p</i> -Methoxystyrene	72	62–69 (1)	92–93 (13) ^a	1.5610	1.5608 ^a
<i>p</i> -Chlorostyrene	55	46–49 (1)	53–56 (3) ^b	1.5654	1.5658 ^b
<i>p</i> -Bromostyrene	71	65–66 (1)	49.5–50.0 (2.5) ^c	1.5950	1.5952 ^c
Phenylcyclopropane	27	38–41 (2)	69 (22) ^d	(1.5311) ^e	(1.5309) ^d
<i>p</i> -Methoxyphenylcyclopropane	2	81–83 (8)	223–224 (745) ^f	1.5331	1.5382 ^f
<i>p</i> -Chlorophenylcyclopropane	12	81–82.5 (7)	86 (8) ^f	1.5521	1.5526 ^f
<i>p</i> -Bromophenylcyclopropane	9	92.5–93 (5)	110–115 (15) ^g	1.5752	1.5508 ^g
			116 (15) ^h		1.5752 ^h
			109–110 (15) ^g		1.5769 ^g

^a R. L. Frank, C. E. Adams, R. E. Allen, R. Gander, and P. V. Smith, *J. Am. Chem. Soc.*, **68**, 1365 (1946). ^b L. A. Brooks, *ibid.*, **66**, 1295 (1944). ^c C. Walling, E. R. Briggs, K. B. Wolfstirn, and F. R. Mayo, *ibid.*, **70**, 1537 (1948). ^d Reference 7. ^e At 25.0°. ^f Reference 48. ^g J. Smejkal, J. Jones, and J. Farkas, *Collection Czech. Chem. Commun.*, **29**, 2950 (1964). ^h R. Ya. Levina and P. A. Gembitskii, *Zh. Obshch. Khim.*, **31**, 3480 (1961).

Table VII. Analytical Results of Substituted Phenylcyclopropanes

Compound	Formula	Carbon, %		Hydrogen, %	
		Calcd	Found	Calcd	Found
Phenylcyclopropane	C ₉ H ₁₀	91.47	91.62	8.53	8.46
<i>p</i> -Methoxyphenylcyclopropane	C ₁₀ H ₁₂ O	81.04	80.80	8.16	8.43
<i>p</i> -Chlorophenylcyclopropane	C ₉ H ₉ Cl	70.83	70.55	5.94	6.09
<i>p</i> -Bromophenylcyclopropane	C ₉ H ₉ Br	54.85	54.55	4.60	4.63
<i>o</i> -Nitrophenylcyclopropane ^a	C ₉ H ₉ NO ₂	66.25	66.49	5.56	5.52
<i>p</i> -Nitrophenylcyclopropane ^b	C ₉ H ₉ NO ₂	66.25	66.49	5.56	5.60
<i>p</i> -Cyclopropylbenzoic acid	C ₁₀ H ₁₀ O ₂	74.05	74.15	6.22	6.18

^a Calcd for C₉H₉NO₂: N, 8.58. Found: N, 8.68. ^b Calcd for C₉H₉NO₂: N, 8.58. Found: N, 8.62.

p-Bromophenylcyclopropane was converted to the corresponding Grignard reagent and the latter treated with powdered Dry Ice in dry ether.⁸ An acidic material was extracted with dilute sodium hydroxide solution; acidification of the aqueous solution gave *p*-cyclopropylbenzoic acid in 60% yield, mp 157.5–158.0° (lit.⁴⁷ 157–158°) after recrystallizations from carbon tetrachloride. From the ether solution, there was obtained a crystalline material in 7% yield, mp 127.5–128.0° [from petroleum ether (bp 42–44°)], which was considered to be *p,p'*-dicyclopropylbiphenyl on the basis of spectroscopic data; particularly, its nmr spectrum showed only an aromatic A₂B₂ pattern and signals due to cyclopropane protons.

Anal. Calcd for C₁₈H₁₈: C, 92.29; H, 7.71. Found: C, 92.06; H, 7.69.

Nitrophenylcyclopropanes were prepared by the nitration of phenylcyclopropane at –40°. After processing in the usual way, the crude reaction product was distilled under the reduced pressure, and a fraction boiling at 112–127° (6 mm) was collected. Two components in the distillate were separated by a preparative vpc (Aerograph Model A-700 with a 6-m silicone grease column at 200°). The major component, a liquid, n_D^{20} 1.5605, was ascertained as *o*-nitrophenylcyclopropane (lit.^{9,48} n_D^{20} 1.5606) by the examination of its infrared and nmr spectra. The minor component solidified on standing, mp 31.5–33.0°, and was characterized as the *para* isomer (lit. mp 32–33°⁹ and 31°⁴⁸) from the spectral data.

All phenylcyclopropanes used for the measurements of dielectric constant were analytically pure; their analytical results are summarized in Table VII.

Apparatus and Measurements. Electric moments were determined in benzene at 25.0°, and in dioxane at 25.0, 35.0, and 45.0°. Benzene was purified by a standard method;⁴⁹ dioxane was freed from acetal and peroxide⁵⁰ and rectified just before the use. Stored dioxane (stoppered and kept in a cold, dark place for a week) had given an erroneous result; a higher dielectric constant was obtained. The solvents used for the measurements had following physical

constants: benzene, bp 80.0–80.1°, n_D^{20} 1.5011, and d_4^{25} 0.87356; dioxane, bp 101.0–101.2°, n_D^{20} 1.4222, d_4^{25} 1.0279.

The dielectric constants were measured at 1.5 Mc with a heterodyne beat apparatus patterned after Chien;¹⁰ the standard condenser used was a Hewlett-Packard Model CDS-100 variable-air condenser. The cell used was similar to one used by Kubo;⁵¹ it was constructed with two platinum cylinders, the outer one was grounded, and they were wrapped with a glass envelope to which were attached the inlet and outlet tubes. The solution was introduced and removed through them by the pressure of dry air; the total volume of the cell was 4.6 ml. The cell was calibrated with purified benzene and the average of a large number of measurements used; the cell constant thus determined was confirmed by measuring the dipole moments of known compounds, such as chlorobenzene, anisole, and nitrobenzene. Densities of the solutions were measured by a 5-ml Ostwald pycnometer. The measurements of the density and the dielectric constant were made on a series of four or five solutions of different concentrations; the resulting dielectric constant (ϵ_{12}) and specific volume (v_{12}) were plotted graphically against the weight fractions of the solute, and intercepts at zero weight fraction of the solute (ϵ_1 and v_1 , obtained by the least-squares treatments) were used in the calculation. The electric polarizations were obtained from bond refraction values given by Vogel¹² and Smyth.¹³ The molar polarization of the solute at infinite dilution (P_2) and the dipole moment (μ) were calculated from known relations.¹¹ The accuracy of the experimental procedures was checked by examining known substances; the dipole moments observed were: chlorobenzene, 1.56 D. (lit.¹⁴ 1.58 D.); nitrobenzene, 3.98 D. (lit.¹⁴ 3.98 D.); anisole, 1.23 D. (lit.¹⁴ 1.25 D.). The dipole moments of substituted phenylcyclopropanes and related data are summarized in Tables I and II.

The standard errors in μ are calculated⁵² and are given in Tables I and II; the errors drawn from the scattering of the points for the specific volume was not considered.^{52,53}

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