[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, THE UNIVERSITY OF CHICAGO]

The Phenyl–Carbon–Phenyl Angle in 1,1-Diphenylcyclopropane[1]

BY M. GOLDSMITH AND G. W. WHELAND

Several recent theoretical[2-4] and experimental[5-7] papers have dealt with the exterior valence angle in cyclopropane. In the experiments which are reported in this present paper the value of the angle in question is determined from the dipole moments of 1,1-bis-(*p*-chlorophenyl)-cyclopropane, 1,1-diphenylcyclopropane and chlorobenzene; the method here employed is, of course, the same as the one which has been previously used for the measurement of the corresponding angles in diphenylmethane[8,9] and 1,1-diphenylethylene.[10] Evidence regarding the direction of the cyclopropyl–phenyl bond moment, discussed by Rogers,[11] has also been obtained.

Experimental

Materials

Benzene.—Eastman Kodak Co. White Label thiophene-free benzene was stored over, and distilled from, sodium hydride. The center cut (b. p. 80.0–80.1° at 760 mm., $n^{20}\text{D}$ 1.501) was redistilled from sodium hydride immediately before use.

***p*-Xylene.**—Eastman White Label *p*-xylene was purified in a manner identical with that described for benzene; b. p. 137.9–138.0° (751 mm.), $n^{20}\text{D}$ 1.496.

Tetrachloroethylene.—Eastman White Label tetrachloroethylene was dried over anhydrous calcium sulfate and fractionated; b. p. 120.8–121.0° (756 mm.), $n^{23.7}\text{D}$ 1.503.

Benzophenone.—Eastman White Label benzophenone was recrystallized from ethanol and from petroleum ether; m. p. 48.0–48.5°.

1,1-Diphenylcyclopropane.—This compound was prepared from 1,1-diphenylethylene and diazomethane by the method of Wieland and Probst.[12] The crude cyclopropane was freed of unreacted olefin by titration with bromine in carbon tetrachloride at 0° and by subsequent fractionation; b. p. 117.0–117.5° (2 mm.), $n^{20}\text{D}$ 1.590.

Anal. Calcd. for $C_{15}H_{14}$: C, 92.73; H, 7.27; mol. wt., 194. Found: C, 92.9; H, 7.3; mol. wt. (f. p. benzene), 193.

1,1-bis-(*p*-Chlorophenyl)-cyclopropane.—This compound was prepared by the reaction of 1,1-bis-(*p*-chlorophenyl)-ethylene with diazomethane. The conditions for this reaction are identical with those for the preparation of 1,1-diphenylcyclopropane. The compound separates from methanol in white needles, m. p. 105.5–106°, and reacts at room temperature neither with bromine in carbon tetrachloride nor with neutral 0.2 *N* potassium permanganate.

Anal. Calcd. for $C_{15}H_{12}Cl_2$: C, 68.45; H, 4.60; Cl, 26.95; mol. wt., 263. Found: C, 68.5; H, 4.5; Cl, 27.0; mol. wt. (f. p. benzene), 260.

1,1-bis-(*p*-Chlorophenyl)-cyclopropane has not been reported previously in the literature. A sample of this compound previously prepared by Mr. Joseph R. Schwartz of this Laboratory proved to be identical with our preparation.

Apparatus

Dielectric Constants.—The circuit diagram of our heterodyne beat apparatus is given in Fig. 1. "Locking in" of the oscillators is rendered negligible at 100 K. C. by the use of very light coupling. Any error due to frequency drift may be eliminated by measurement of the zero beat capacitance of the variable frequency oscillator both with and without the test condenser in the circuit. The test cell, which had a volume of 10 cc. and a capacitance of 80 $\mu\mu$ f., was constructed according to Fairbrother's design[13] and was calibrated, at each temperature at which dielectric constants were measured, in the manner described[13] by him.

Temperatures.—The temperatures at which measurements were made were maintained, with a maximum variation of 0.03°, in an oil thermostat.

Densities.—The densities of the solutions were measured with a modified Ostwald Sprengel pycnometer which was calibrated at the temperatures below 80° with distilled water. The volume of the pycnometer at 98.6°, and at 122.0°, was obtained by extrapolation.

Refractive Indices.—Measurements were made with a refractometer of the Abbé type.

Experimental Results

Optical Determinations.—Values of the mole fractions f_2 of the solutes, the dielectric constants ϵ of the solutions, the densities d of the solutions, and the total molar polarizations P_1 and P_2, of the solvents and solutes, respectively, are given in Table I for some typical measurements. Table II contains the values of P_2^∞, the total molar polarizations of the solutes at infinite dilution, obtained by graphical extrapolation; the values of the molecular refractions for the sodium D lines $MR\text{D}$ of the solutes; and the values of the dipole moments μ calculated from the formula

$$\mu = 0.0128\sqrt{[P_2^\infty - 1.05(MR\text{D})]T}\ D$$

Temperature Variation Determinations.—Table III contains values of P_2^∞ measured at a series of absolute temperatures T in tetrachloroethylene and in *p*-xylene. Equations of the form

$$P_2^\infty = A + B/T$$

were obtained by the method of least squares. The respective values of A and B are given in Table IV.

Discussion of Results

The dipole moment of benzophenone was measured as a test of our experimental technique. Our optical value 2.97 D agrees well with the value

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(1) An abstract of the thesis submitted by Mark Goldsmith in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Coulson and Mofitt, *J. Chem. Phys.*, **15**, 151 (1947).

(3) Duffey, *ibid.*, **14**, 342 (1946).

(4) Kilpatrick and Spitzer, *ibid.*, **14**, 463 (1946).

(5) Spinrad, THIS JOURNAL, **68**, 617 (1946).

(6) O'Gorman and Schomaker, *ibid.*, **68**, 1138 (1946).

(7) Hassel and Viervoll, *Acta Chem. Scand.*, **1**, 149 (1947).

(8) Bergmann, Engel and Wolff, *Z. physik. Chem.*, **B17**, 81 (1932).

(9) Hampson, Farmer and Sutton, *Proc. Roy. Soc.* (*London*). **A143**, 147 (1934).

(10) Coates and Sutton, *J. Chem. Soc.*, 567 (1942).

(11) Rogers, THIS JOURNAL, **69**, 2544 (1947).

(12) Wieland and Probst, *Ann.*, **530**, 274 (1937).

(13) Fairbrother, *Proc. Roy. Soc.* (*London*). **A142**, 173 (1933).

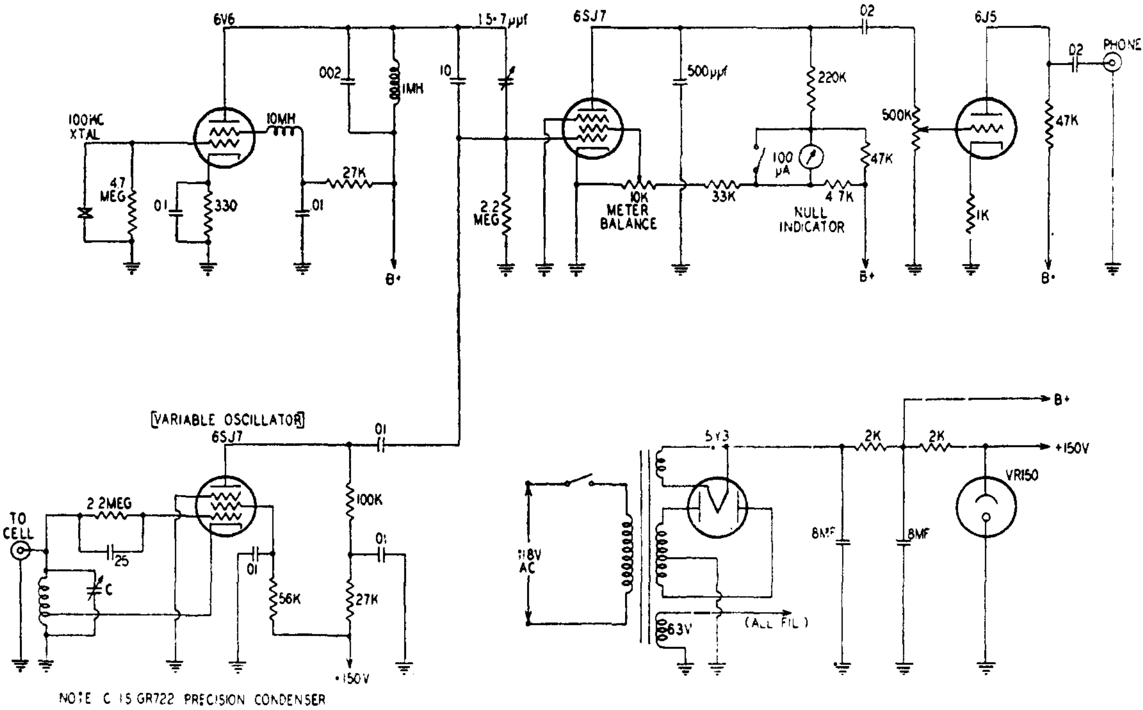

Fig. 1.—Heterodyne beat apparatus.

TABLE I

DIELECTRIC CONSTANTS, DENSITIES AND POLARIZATIONS

f_2	ϵ	d	P_2
	$C_{15}H_{12}Cl_2$ in Benzene (23.7°)		
0	2.275	0.8742	(P_1 = 26.65)
0.03302	2.487	.9010	158
.02224	2.421	.8926	160
.01878	2.396	.8897	158
.01451	2.371	.8863	161
.009852	2.342	.8827	162
	$C_{15}H_{14}$ in *p*-Xylene (23.7°)		
0	2.263	0.8575	(P_1 = 36.68)
0.02929	2.281	.8655	67
.02428	2.280	.8642	70
.01551	2.273	.8618	68
.01239	2.271	.8610	69
.01227	2.270	.8609	67
	Benzophenone in *p*-Xylene (30.6°)		
0	2.250	0.8517	(P_1 = 36.67)
0.02763	2.499	.8612	225
.01412	2.378	.8566	230
.009251	2.334	.8548	233

2.98 *D* which is the average of twelve optical-solution values reported[14] in the literature.

The temperature variation values of the dipole moment of 1,1-bis-(*p*-chlorophenyl)-cyclopropane are in poor agreement with the values (Table II) obtained by the optical method. Presumably, these discrepancies are due, at least in part, to a variation of the solvent effect with temperature.[15]

TABLE II

OPTICAL DETERMINATIONS OF DIPOLE MOMENTS

Compound	P_2^∞	MR_D[a]	T, °K.	μ	Solvent
$C_{15}H_{12}Cl_2$	163	73	296.8	2.05	Benzene
$C_{15}H_{12}Cl_2$	158	73	296.8	1.99	Tetrachloroethylene
$C_{15}H_{12}Cl_2$	158	73	303.7	2.01	*p*-Xylene
$C_{15}H_{14}$	69	63	296.8	0.2–0.5	*p*-Xylene
Benzophenone	237	57[b]	303.7	2.97	*p*-Xylene

[a] These values of the molecular refraction were measured in the solvents stated, with f_2, the mole fraction of the solute, in the range 0.01–0.02. [b] Auwers and Eisenlohr, *J. prakt. Chem.*, **84**, 37 (1911).

TABLE III

VARIATION OF POLARIZATION WITH TEMPERATURE

$C_{15}H_{12}Cl_2$ in *p*-xylene		$C_{15}H_{12}Cl_2$ in C_2Cl_4		Benzophenone in *p*-xylene	
$1/T \times 10^3$	P_2^∞	$1/T \times 10^3$	P_2^∞	$1/T \times 10^3$	P_2^∞
3.293	158	3.369	158	3.293	237
2.995	149	3.182	154	2.995	220
2.839	147	2.995	149	2.839	209
2.690	146	2.839	145	2.690	204
2.531	145	2.690	145	2.531	197

TABLE IV

TEMPERATURE VARIATION DETERMINATIONS OF DIPOLE MOMENTS

Compound	Solvent	A	$B \times 10^{-4}$	μ	Temp. range. °C.
$C_{15}H_{12}Cl_2$	C_2Cl_4	83.6	2.18	1.89	23.7– 98.6
$C_{15}H_{12}Cl_2$	*p*-Xylene	102	1.68	1.66	30.6–122.0
Benzophenone	*p*-Xylene	52.6	5.58	3.02	30.6–122.0

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[14] *Trans. Faraday Soc.*, **30**, Appendix (1934).

[15] Glasstone, *Ann. Reports Chem. Soc.*, **33**, 117 (1936).

The possibility that the discrepancies are primarily due instead to unexpectedly large atom polarizations seems unlikely for two reasons. First, with compounds, such as *p*-benzoquinone, which do have large atom polarizations, the sum *A* of the electronic and atom polarizations is essentially independent of solvent[16]; with 1,1-bis-(*p*-chlorophenyl)-cyclopropane, on the other hand, *A* is 18.4 cc. per mole greater in *p*-xylene than it is in tetrachloroethylene (Table IV). Second, the atom polarizations of several closely analogous compounds, such as *p*-bromophenyl ether, are evidently small since, with these substances, the sums of the atom plus orientation polarizations have been found to be of the order of only 10 cc. per mole.[17] For these reasons, the optical values will be accepted in preference to the temperature variation ones, and the dipole moment of 1,1-bis-(*p*-chlorophenyl)-cyclopropane will be taken as 2.02 ± 0.03 *D*.

The phenyl–carbon–phenyl angle, θ, may be calculated in the manner previously described[9] by Sutton and his co-workers. If it is assumed that the optical-solution value of the dipole moment of chlorobenzene[14] is 1.57 *D*, and that the cyclopropylidene-phenyl and phenyl–chlorine bond moments are in the same direction, the angle θ is found to be equal to $116 \pm 10°$. If it is instead assumed that these bond moments are in opposite directions, the angle is found to be $81 \pm 10°$. A value of θ which is almost 30° less than the normal tetrahedral angle is improbable. It is therefore considered that θ is equal to $116 \pm 10°$; this conclusion supports the value, $112 \pm 4°$, assigned by electron diffraction to the Cl–C–Cl angle[8] in 1,1-dichlorocyclopropane. (The limits of error cited above are based merely on the internal consistency of the optical measurements reported in this paper. The true limits of error, as in all analogous measurements of bond angles, must be somewhat greater when allowance is made for the uncertainty in the value of the atom polarization and in the moment of chlorobenzene, and for the possibility of variations in bond angles, in bond moments, and in the solvent effect.)

Acknowledgments.—The authors are indebted to Messrs. P. R. Bell, Jr.,[18] and P. Shevick[19] for the design and construction of the heterodyne beat apparatus, and to Mr. W. Saschek and Mr. D. E. Mann of this Laboratory for their aid and suggestions.

Summary

The dipole moments of 1,1-bis-(*p*-chlorophenyl)-cyclopropane and 1,1-diphenylcyclopropane have been measured.

The phenyl–carbon–phenyl angle in 1,1-diphenylcyclopropane has been estimated as $116 \pm 10°$.

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[16] *Cf.* Finn, Hampson and Sutton, *J. Chem. Soc.*, 1254 (1938); Hammick, Hampson and Jenkins, *ibid.*, 1263 (1938); Coop and Sutton, *ibid.*, 1269 (1938).

[17] Coop and Sutton, *J. Chem. Soc.*, 1869 (1938).

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[19] Nuclear Physics Institute, University of Chicago.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

Quadridentate Amines. I. Some Coördination Compounds of Cobalt(III) and Triethylenetetramine[1]

BY FRED BASOLO

It was first shown by Mann[2] and later by Morgan and Burstall[3] that certain tetramines are capable of behaving as quadridentate donors to form complex inorganic compounds of cobalt(III). Mann[2] used β,β',β''-triaminotriethylamine and obtained *cis*-[Co tren(SCN)$_2$]SCN. Because of the structure of this amine, the corresponding *trans*-salt is sterically too unstable to exist. The amine used by Morgan and Burstall[3] was 2,2′,2″,2‴-tetrapyridyl and yielded *trans*-[Co tetrpyCl$_2$]Cl. They point out that the pyridine rings of the coordinated tetrapyridyl must remain in the same plane, and therefore the chloro groups must be in *trans*-positions. In both of these investigations the analyses of the resulting compounds agreed with those calculated for the respective compounds, but in neither case was any attempt made to establish conclusively the configuration of the complex cation.

More recently, Jonassen, Dexter and Douglas[4] have studied the complexes formed between triethylenetetramine and copper(II) and nickel(II) ions in water solution. They found that triethylenetetramine behaves as a quadridentate amine. The present work was undertaken to determine whether coördination compounds of triethylenetetramine and cobalt(III) can be isolated and also to study the configuration and stability of these compounds.

The dichlorotriethylenetetraminecobalt(III) ion can theoretically exist in three stereoisomeric forms

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[1] Presented before the Physical and Inorganic Division at the 113th meeting of the American Chemical Society, Chicago, Ill., April 19–23, 1948.

[2] Mann, *J. Chem. Soc.*, 409 (1929).

[3] Morgan and Burstall, *ibid.*, 1672 (1938).

[4] Reported by Jonassen, Dexter and Douglas at the 112th meeting of the American Chemical Society.