622. *Polarisation in Conjugated Systems. Part I. The Refractions and Electric Dipole Moments of Some Derivatives of Benzene, Styrene, Diphenyl, Stilbene, and 1 : 4-Diphenylbutadiene.*

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The dipole moments of 44 compounds have been measured in order further to elucidate the nature of the polarisation which takes place when one or more groups are substituted into a conjugated system. Part I contains all the experimental observations. The theoretical difficulties involved in estimating distortion polarisations of compounds having large dispersions are discussed; it is suggested that the use of the so-called "calculated" $[R]_D$ values is less hazardous than that of the observed ones in such cases.

Comparison is made, when possible, between dipole moments already published and those now reported. The choice of dipole moment values from the literature is considered; and a critical list for simple benzene and paraffin derivatives is given.

It is concluded that styrene probably has a moment of *ca.* 0·1 D., and that 2 : 4 : 6-trimethylstilbene and triphenylethylene may not be quite non-polar. In the last two compounds there is evidence that conjugation is sterically inhibited.

This investigation began in 1948 when we were invited by the Chester Beatty Research Institute, Royal Cancer Hospital, London, to measure the electric dipole moments of a large number of rare compounds. Most of them were derivatives of stilbene which had been synthesised because of their physiological interest: several are either carcinogenic or inhibit the growth of tumours, according to the experimental conditions (Haddow, Harris, Kon, and Roe, *Phil. Trans.*, 1948, *A*, **241**, 147).

One purpose of the investigation was to add to the physical chemistry of these important compounds, in an attempt to bring to light any chemicophysiological relations. Related information (spectroscopic, etc.) has already been, or is about to be, published (Haddow *et al.*, *loc. cit.*; Thompson, Vago, Corfield, and Orr, *J.*, 1950, 214; Coulson and Jacobs, *J.*, 1949, 1983; Pullman, *Compt. rend.*, 1948, **226**, 486; Butler, *Nature*, 1950, **166**, 18; Beale and Liberman, to be published).

However, this aspect of the work is treated only incidentally here; the emphasis is on physicochemical problems. It was expected that the moments of some compounds would throw light on several interesting topics covered by the general title. As the investigation proceeded, it was found that certain questions were incompletely answered; so other compounds—mostly derivatives of styrene and diphenyl—were prepared.

Among the topics discussed in detail later are the dependence of the polarisation of a conjugated system, bearing a polar group, on: (i) the nature of the system (Part IV) and of the group (Part V), (ii) the position of attachment (Part III), and (iii) the presence in the molecule of other groups capable of steric interaction (Part II) or electronic interaction (Part VI).

This paper contains all the experimental details, including some optical-dispersion measurements. It was found at the outset of the work that the measured refractions of the more highly conjugated compounds were appreciably greater than those calculated by adding the refractions of the constituent fragments of the molecules. The disparity was too large to be ignored, since the resulting uncertainty in the dipole moments was in some cases about ten times the experimental error. It arises from the unusually large dispersions shown by molecules with such extensive conjugated systems; and the dispersion measurements were undertaken in order to find how the distortion polarisations could best be estimated in the peculiar circumstances.

The dipole moments which have been obtained are compared with any previously reported values; and a critical list of moments needed in the later discussion is given, with some notes on the selection of such data.

Finally, the values found for the moments of stilbene, 2 : 4 : 6-trimethylstilbene, and triphenylethylene are discussed.

EXPERIMENTAL.

Preparation and Purification of Materials.—Benzene. This was purified in the usual way (Everard and Sutton, *J.*, 1949, 2312).

Styrene. A B.D.H. specimen was dried ($CaCl_2$) and twice fractionated in a vacuum; the fraction of b. p. 36·5—37°/11 mm. was collected and used the same day. Beilstein's "Handbuch" (1st revision) quotes b. p. 34·2°/10 mm. and b. p. 40°/14 mm.

Benzonitrile. Fractionation of two different commercial specimens having given an unsatisfactory product, the material was made from pure benzamide (m. p. 127—128°) by heating it with phosphoric anhydride for 15 minutes and distilling the product (Buckton and Hofmann, *J.*, 1857, **9**, 255). The distillate, which melted at −14°, was redistilled over phosphoric anhydride at 192—193°, and then had m. p. −13·1° to −13·6° (Weissberger and Proskauer, "Organic Solvents," O.U.P., 1935, p. 75, give −13·1°). Before use four-fifths were slowly frozen and the rest decanted.

p-*Phenylenediamine.* A B.D.H. specimen was recrystallised from ether, water, and benzene–ethanol. It then melted at 141—142° (corr.). Beilstein's "Handbuch" (2nd revision) quotes 142°.

NNN'N'-*Tetramethyl*-p-*phenylenediamine.* The hydrochloride (B.D.H.) was treated with sodium hydroxide solution and warmed, and the product filtered off. The dry precipitate was thrice sublimed in a vacuum, whereafter it had m. p. 48·5—49°. Beilstein's "Handbuch" (2nd revision) quotes 50—51°.

4-*Chlorostyrene.* This was prepared from *p*-chloroacetophenone by reduction and then dehydration. A solution of the phenone (50 g., 0·32 mole) in ether (100 ml.) was added gradually with cooling to ethereal lithium aluminium hydride (250 ml.) (≡ 0·65 mole of hydrogen) (cf. Finholt, Bond, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 1199), and the mixture agitated for 15 minutes. Dilute hydrochloric acid was then cautiously added until a clear aqueous layer was obtained. The ethereal layer was separated and, together with an ethereal extract of the aqueous layer, was dried ($MgSO_4$) and evaporated. The residual oil on distillation afforded 1-*p*-chlorophenylethanol (42 g.), b. p. 87—87·5°/1 mm. (Found: C, 60·9; H, 6·1; Cl, 22·4. Calc. for C_8H_9OCl: C, 61·3; H, 5·8; Cl, 22·6%).

Potassium hydrogen sulphate (3·5 g.) and quinol (0·5 g.) were fused at 210—220° in a 25-ml. Claisen flask immersed in an oil-bath. Nitrogen, purified by passing successively through pyrogallol solution, concentrated sulphuric acid, and tubes containing potassium hydroxide pellets, was introduced below the surface of the melt, and a pressure of 90—100 mm. maintained over it. 1-*p*-Chlorophenylethanol (8 g.) was added at the rate of 1 drop/sec. The distillate, dissolved in peroxide-free ether, was washed with 5% sodium hydroxide solution and saturated calcium chloride solution, and dried ($CaCl_2$). Quinol (0·5 g.) in ether was added, the ether distilled off in a nitrogen atmosphere, clean all-glass apparatus being used, and the styrene fractionated with a 4-plate Dufton column (cf. Marvel and Schertz, *J. Amer. Chem. Soc.*, 1943, **65**, 2054; Brooks, *ibid.*, 1944, **66**, 1295). The fraction (2·5 g.) of b. p. 73·5—74·5°/6—7 mm. was used.

4-*Bromostyrene.* This was prepared similarly. 1-*p*-Bromophenylethanol was obtained as a colourless oil, b. p. 115—118°/1—2 mm. (Found: C, 48·1; H, 4·5; Br, 39·5. Calc. for C_8H_9OBr: C, 47·8; H, 4·5; Br, 39·8%), and 4-bromostyrene as an almost colourless oil, b. p. 94—95°/4—5 mm. (Found: C, 52·6; H, 4·1; Br, 43·5. Calc. for C_8H_7Br: C, 52·5; H, 3·8; Br, 43·7%).

The b. p.s of 4-chlorostyrene and 4-bromostyrene are markedly higher than those reported in the literature. These discrepancies were discovered only in the last stages of the preparation of the paper, and they have not yet been elucidated. It is therefore best that the dipole moments of these compounds should be regarded as provisional.

4-*Nitrostyrene.* This compound, prepared according to Strassburg, Gregg, and Walling (*J. Amer. Chem. Soc.*, 1947, **69**, 2141), had the same m. p., 21·4°, as they observed (Found: C, 64·5; H, 4·9; N, 9·4. Calc. for $C_8H_7O_2N$: C, 64·4; H, 4·7; N, 9·4%).

4-*Dimethylaminostyrene.* This was prepared similarly, except that it was recovered pure from its ethereal solution as described above for 4-chlorostyrene. It had m. p. 16·5° (Strassburg *et al.*, *loc. cit.*, give 16·8°).

β-Nitrostyrene. A B.D.H. specimen, twice recrystallised from ligroin, had m. p. 57—57·5° (Beilstein's "Handbuch" quotes 58°).

Benzidine. "AnalaR" material was twice recrystallised from ethanol and sublimed in a vacuum; it had m. p. 125° (Kofler and Lindpaintner, *Mikrochem.*, 1938, **24**, 43, give m. p. 125° *inter al.*).

NNN'N'-*Tetramethylbenzidine.* This was prepared by oxidising dimethylaniline (Willstätter and Kalb, *Ber.*, 1904, **37**, 3761). It was purified by being recrystallised twice from benzene and thrice from amyl alcohol, and finally sublimed in a vacuum. It had m. p. 195—196° (corr.); Beilstein's "Handbuch" quotes 193·5°, 195°, 197°, and 198°.

4-*Cyanodiphenyl.* This compound was made by the Sandmeyer reaction (cf. Kaiser, *Annalen*, 1890, **257**, 100) and was then recrystallised from ethanol to constant m. p., 86—86·5°; Beilstein's "Handbuch" (2nd revision) quotes 82° and 88°.

4-*Bromodiphenyl.* This was made and purified similarly. It had m. p. 88·5°; Beilstein's "Handbuch" (2nd revision) quotes 89—90° and 91·2°.

4-*Nitrodiphenyl.* A B.D.H. specimen, twice recrystallised from ethanol, melted at 113·5—114° (corr.); Beilstein's "Handbuch" (2nd revision) quotes 114—115°.

4-Dimethylaminodiphenyl. B.D.H. 4-aminodiphenyl was methylated by Bell and Kenyon's method (*J.*, 1926, 2705). The product was twice recrystallised from ethanol, and then thrice more without change of m. p., 120° (corr.); Bell and Kenyon give 123°, and Evans and Williams (*J.*, 1939, 1199) give 122°.

Stilbene. Stilbene was purified by three recrystallisations from ethanol followed by vacuum sublimation.

The remaining compounds were obtained from the Chester Beatty Research Institute. They had been prepared as described by Haddow, Harris, Kon, and Roe (*loc. cit.*), and were purified by chromatography and recrystallisation as also described there, either in Oxford or at the Institute, not more than *ca.* 1 month before examination. Light was excluded from the materials during storage and (except for red or dim white light) until dielectric-constant measurements had been completed on the solutions, owing to the danger of isomerisation; there was no evidence that this ever occurred during measurements.

The following special details may be noted. 4-Bromostilbene was found to be particularly unstable, and was recrystallised from ethanol immediately before examination. Triphenylethylene, though scrupulously purified, had a rather low m. p., but was spectroscopically pure. Spectroscopic examination also showed that the 1-*p*-dimethylaminophenyl-4-phenylbuta-1 : 3-diene used was the *trans-trans*-isomer (R. N. Beale, private communication). It is assumed from the method of preparation, and confirmed in many cases by the spectra, that all the compounds examined had *trans*-configurations (except *cis*-4-bromo-4′-nitrostilbene).

The m. p.s of the specimens used were as follows; they are uncorrected unless italicised The numerals in Clarendon type denote the names of the compounds as given in Tables V and VI: **2**, 141—142°; **3**, 106°; **4**, 119°; **5**, 150°; **6**, 116°; **7**, 55°; **8**, 76—77°; **9**, 131—132°; **10**, 78—79°; **11**, 84—85°; **12**, 154—155°; **13**, 175—176°; **28**, *213—214°*; **29**, 138°; **30**, 81°; **31**, *200°*; **32**, *105°*; **33**, *220°*; **34**, *72°*; **35**, *98—99°*; **36**, 149°; **37**, *79°*; **38**, *255°*; **39**, *78·5—79°*; **40**, *133°*; **41**, *124°*; **42**, *51·5—52°*; **43**, 70°; **44**, *181—182°*.

Physical Measurements.—As many of the substances were available in only 0·1-g. quantities, the small-scale technique developed by Everard and Sutton (*J.*, 1951, 16) was widely employed. For the other substances the older apparatus for 1-g. quantities was used. Descriptions of, or references to, procedure will be found in the paper just cited.

In several cases, because of the insolubility of the solute, it was necessary to warm judiciously the closed vessel containing the two phases, then to cool it rapidly to *ca.* 25° and to make the dielectric-constant measurement. In this way observations could be made on somewhat supersaturated solutions.

Because they were made on dilute solutions, the accuracy of the dispersion measurements is less than could have been attained if such measurements had been the sole object of examining the compounds. Since, however, this was a subsidiary object, we were content (and often compelled) to sacrifice some accuracy so as to save time and materials. We draw conclusions only from the dispersion data as a whole, but not from any particular measurement.

Refractive-index values for solutions of compounds **1**—**13** were measured with an interferometer and later found erroneous (see Everard, Hill, and Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417), but a Pulfrich refractometer with divided cell was used for the remaining compounds, except benzonitrile.

Polarisations, refractions, dispersions, and dipole moments were computed as described by Everard and Sutton (*J.*, 1951, 16), except that "calculated" values of $[R]_D$ were used for the distortion polarisations (see Discussion); these were based on data in Landolt–Börnstein's "Tabellen" (both the original work and supplementary volumes), and the following $[R]_D$ values: styrene, 36·49 ("Selected Values

TABLE I.*

Compd.	$10^6\omega$.	ε.	v.
1	4,092	2·2730	1·14483
	8,179	2·2737	1·14467
	14,703	2·2744	1·14450
	20,149	2·2750	1·14432
2	1,321	2·2800	1·14479
	2,089	2·2841	1·14454
	7,922	2·3154	1·14313
	8,714	2·3199	1·14301
3	641	2·2738	1·14486
	1,707	2·2755	1·14458
	2,327	2·2765	1·14446
	4,241	2·2798	1·14408
4	1,077	2·2742	1·14477
	3,716	2·2790	1·14406
	7,448	2·2861	1·14309
	8,815	2·2880	1·14280
5	1,927	2·2782	1·14436
	2,917	2·2808	1·14431
	6,068	2·2898	1·14345
	8,321	2·2963	1·14301
6	603	2·2796	1·14527
	1,724	2·2910	1·14493
	2,454	2·2993	1·14471
	4,409	2·3204	1·14427
7	1,597	2·2742	—
	1,758	2·2748	1·14475
	3,108	2·2758	1·14444
	4,676	2·2773	1·14424
	9,238	2·2813	1·14345
8	1,146	2·2750	1·14474
	1,727	2·2758	1·14462
	5,310	2·2822	1·14392
	6,778	2·2848	1·14361
9	1,386	2·2765	1·14497
	4,923	2·2863	1·14428
	6,131	2·2893	1·14406
	9,058	2·2971	1·14353
10	1,212	2·2762	1·14490
	2,104	2·2788	1·14458
	5,380	2·2888	1·14407
	8,984	2·2992	1·14347
11	960	2·2762	1·14496
	3,598	2·2845	1·14445
	4,789	2·2885	1·14424
	10,243	2·3062	1·14324
12	723	2·2801	—
	741	2·2802	1·14479
	1,319	2·2864	1·14463
	2,471	2·2984	1·14432
	3,861	2·3125	1·14396
13	897	2·2814	1·14470
	1,739	2·2902	1·14446
	2,181	2·2953	1·14430
	2,944	2·3030	1·14406

* For an explanation of the method of presentation in Tables I—VI, see p. 2811.

TABLE II.

Compd.	Soln.	$10^6\omega$.	ε.	v.	$10^5\Delta n_D$.
14	1	1,947	2·3067	1·14434	7
	2	2,937	2·3231	1·14413	10
	3	6,835	2·3915	1·14362	21
	4	9,806	2·4423	1·14317	32
15	1	902	2·2752	1·14632	—
	2	1,879	2·2781	1·14592	—
	3	2,440	—	1·14583	26
	4	3,833	2·2840	—	40
	5	4,262	2·2851	—	45
16	1	1,836	2·2745	1·14585	6
	2	12,533	2·2850	1·14465	81
	3	15,960	2·2887	1·14422	102
17	1	977	2·2734	1·14419	12
	2	3,771	2·2776	1·14320	25
	3	4,397	2·2791	1·14293	—
	4	14,254	2·2939	1·13865	69
18	1	3,630	2·2792	1·14392	—
	2	3,925	2·2803	1·14389	30
	3	17,201	2·3058	1·14080	104
	4	23,107	2·3163	1·13982	—
19	1	1,776	2·2794	1·14441	—
	2	5,371	2·2929	1·14398	53
	3	5,486	2·2930	1·14389	53
	4	6,338	2·2960	1·14383	64
20	1	1,632	2·2968	1·14597	17
	2	4,058	2·3330	1·14513	34
	3	8,026	2·3931	1·14386	79
21	1	1,142	2·2877	1·14431	8
	2	5,728	2·3483	1·14302	—
	3	6,377	2·3568	1·14284	41
22	1	340	2·2734	1·14644	—
	2	2,368	2·2777	1·14577	—
	3	5,660	—	—	101
	4	6,975	2·2865	1·14442	120
	5	7,146	2·2865	1·14435	131
23	1	3,543	2·2780	1·14314	—
	2	10,850	2·2890	1·13994	92
	3	14,866	2·2952	1·13827	134
24	1	2,053	2·2959	1·14413	16
	2	7,409	2·3585	1·14284	75
	3	11,369	2·4047	1·14182	116
25	1	1,424	2·2766	1·14428	18
	2	6,421	2·2892	1·14335	82
	3	10,752	2·3008	1·14254	137
26	1	328	2·2767	1·14621	10
	2	6,193	2·3406	1·14428	64
	3	8,429	2·3651	1·14338	96
27	1	3,035	2·2755	1·14598	—
	2	4,742	2·2773	1·14565	64
	3	11,083	2·2838	1·14427	166
	4	13,396	2·2859	1·14372	190
28	1	1,130	2·2790	1·14601	17
	2	1,375	2·2803	1·14577	22
	3	4,222	2·2956	1·14451	71
	4	6,202	2·3067	1·14354	112
29	1	2,490	2·2768	1·14423	—
	2	4,673	2·2799	1·14341	—
	3	7,279	2·2836	1·14218	—
	4	8,652	—	—	99
	5	9,119	2·2866	1·14159	—
30	1	2,589	2·2920	1·14403	—
	2	3,260	2·2969	1·14357	—
	3	8,936	2·3403	1·14091	98
	4	10,121	2·3492	1·14038	109
31	1	1,121	2·2770	1·14404	27
	2	5,061	2·2920	1·14218	83
	3	8,895	2·3065	1·14042	148
	4	11,315	2·3156	1·13916	—
32	1	1,500	2·2776	1·14410	29
	2	9,207	2·3035	1·14200	184
	3	11,555	2·3114	1·14131	214
33	1	1,560	2·2842	1·14425	29
	2	6,301	2·3180	1·14290	119
	3	7,864	2·3297	1·14236	157
34	1	4,177	2·3117	1·14365	54
35	1	2,419	2·2811	1·14416	47
	2	10,334	2·3089	1·14284	190
	3	11,987	2·3143	1·14254	217
36	1	956	2·2762	1·14516	—
	2	2,071	2·2797	1·14473	—
	3	2,964	2·2824	1·14475	—
	4	4,213	2·2862	1·14439	—
	5	7,932	2·2985	1·14375	—
	6	9,097	—	—	183
37	1	1,812	2·2774	1·14422	28
	2	7,245	2·2913	1·14332	109
	3	9,099	2·2960	1·14299	—
	4	19,835	—	—	300
38	1	243	2·2779	1·14450	—
	2	877	2·2924	1·14428	32
	3	1,098	2·2976	1·14419	35
39	1	792	2·2745	1·14447	11
	2	6,273	2·2863	1·14347	88
	3	8,311	2·2908	1·14305	117
40	1	795	2·2835	1·14431	—
	2	4,764	2·3360	1·14293	93
	3	5,633	2·3479	1·14269	106
41	1	2,368	2·2736	1·14606	41
	2	2,923	2·2736	1·14597	48
	3	15,629	2·2787	1·14344	238
	4	18,333	2·2799	1·14302	281
42	1	1,187	2·2733	1·14438	14
	2	6,815	2·2749	1·14356	71
	3	8,979	2·2758	1·14329	93
43	1	4,317	2·2742	1·14423	—
	2	7,156	2·2756	1·14344	—
	3	14,432	2·2789	1·14182	210
	4	20,861	2·2815	1·14038	312
44	1	1,094	2·2767	1·14609	32
	2	1,265	2·2773	1·14618	35
	3	2,040	2·2799	1·14600	57
	4	3,642	2·2854	1·14573	95

of Properties of Hydrocarbons," U.S. Govt. Printing Office, 1947); diphenyl, 52·41 (von Auwers and Frühling, *Annalen*, 1921, **422**, 192); *trans*-stilbene, 65·60, and *cis*-stilbene, 61·77 (von Auwers, *Ber.*, 1935, **68**, 1346); and *trans-trans*-1 : 4-diphenylbuta-1 : 3-diene, 85 c.c. The last value has been interpolated from $[R]_{\alpha}$ and $[R]_{\beta}$ given by Smedley (*J.*, 1908, **93**, 372), and is subject to an uncertainty of *ca.* ±2 c.c. Everard, Hill, and Sutton (*loc. cit.*) inadvertently calculated $[R]_D$ values for the 4-nitro- and 4-dimethylamino-derivatives of 1 : 4-diphenylbutadiene from the refraction of the *cis-cis*-hydro-

TABLE III.

		$10^5\Delta n_\lambda$.					$[R]_\lambda$.					
Compd.	Soln.	λ : 6438.	5461.	5086.	4800.	4358.	6438.	5893.	5461.	5086.	4800.	4358.
20	3	79	89	95	97	123	43·6	43·7	45·1	46·0	46·7	49·6
22	3	103	108	112	114	117	64·4	64·4	65·9	66·9	67·5	68·6
25	3	130	139	148	155	180	68·3	69·4	69·9	71·2	72·3	75·7
26	3	90	93	99	104	118	58·5	59·5	59·4	60·6	61·5	64·0
27	3	154	173	182	191	221	84·1	86·1	87·2	88·9	90·2	94·7
27	4	184	200	214	221	244	83·8	84·9	86·2	88·0	89·3	92·4
28	4	109	115	127	134	144	81·2	82·1	83·1	86·6	88·5	91·7
29	4	90	104	104	112	118	71·0	72·8	74·0	74·4	76·1	78·0
30	4	101	118	121	126	148	76·4	78·2	80·1	80·9	82·2	86·6
31	3	142	160	170	193	—	86·8	88·2	90·6	93·2	98·0	—
32	3	200	241	258	284	354	92·4	92·7	96·4	99·0	102·6	112·1
33	3	147	171	188	211	269	91·7	94·0	97·0	100·4	105·1	116·6
35	3	209	233	262	288	383	96·2	97·6	99·9	103·8	107·4	119·3
36	6	175	199	211	230	292	86·5	87·8	90·5	92·5	95·5	104·8
37	4	285	314	340	—	458	91·9	93·4	94·8	97·1	—	106·9
39	3	105	121	131	140	164	93·6	96·3	97·4	99·7	101·9	107·1
41	4	267	290	295	311	—	64·9	66·0	66·7	67·3	68·6	—
42	3	90	91	98	95	103	77·9	78·8	78·9	80·4	80·3	82·4
43	4	307	322	331	338	381	89·9	90·6	91·7	92·9	93·8	97·6
44	3	—	—	—	—	117	—	111·9	—	—	—	155·4
44	4	85	101	119	132	—	104·9	109·3	112·2	117·4	124·9	—

TABLE IV.

Compd.	$[R]_D$, obs.	$[R]_D$, calc.	$E[R]_D$.	D ⟵	±	⟶ $[R]_\infty$.	$[R]_D$, calc., $-[R]_\infty$.
14	32·2	—	—	—	—	—	—
15	33·2	35·0	−1·8	—	—	—	—
16	55·7	55·5	0·2	—	—	—	—
17	43·9	44·3	−0·4	—	—	—	—
18	42·5	41·7	0·8	—	—	—	—
19	52·3	51·2	1·1	—	—	—	—
20	43·6	43·1	0·5	4·8	1	38·8	4·3
21	43·1	43·1	0	—	—	—	—
22	64·6	61·3	3·3	4·7	1	59·9	1·4
23	60·5	60·2	0·3	—	—	—	—
24	57·6	57·8	−0·2	—	—	—	—
25	69·4	67·1	2·3	5·8	1	63·6	3·5
26	58·8	59·0	−0·2	5·0	1·5	53·8	5·2
27	85·3	81·7	3·6	7·5	0·3	77·8	3·5
28	82·1	77·8	4·3	9·5	1·5	72·6	5·2
29	72·8	73·4	−0·6	6·4	1	66·4	7·0
30	78·0	76·2	1·8	7·6	1	70·4	5·8
31	87·4	80·0	7·4	10·6	2	76·8	3·2
32	93·3	85·5	7·8	12·3	2	81·0	4·5
33	93·6	85·5	8·1	14·3	1·5	79·3	6·2
34	~69·4	71·0	−1·6	—	—	—	—
35	97·6	89·7	7·9	13·2	2	84·4	5·3
36	87·8	80·3	7·5	9·6	1·5	78·2	2·1
37	93·4	90·1	3·3	8·3	1	85·1	5·0
38	~114	86·9	27	—	—	—	—
39	96·3	94·7	1·6	10·8	0·5	85·5	9·2
40	~88·2	79·1	9·1	—	—	—	—
41	65·8	(59·2)	(6·6)	4·4	0·5	61·4	(−2·2)
42	78·7	80·0	−1·3	3·7	1	75·0	5·0
43	90·6	90·7	−0·1	5·6	0·5	85·0	5·7
44	109·1	99·7	9·4	14·3	4	94·8	4·9

carbon, instead of the *trans-trans* one. The distortion polarisation used for 4-dimethylamino-2′ : 4′ : 6′-trimethylstilbene was based on $[R]_D$ for 2 : 4 : 6-trimethylstilbene.

The uncertainties in the dipole-moment values caused by errors in experimental observation only are estimated not to exceed ±0·02 D., save for 2-dimethylaminostilbene (±0·05 D.), 3-cyanostilbene, of which only enough to make up one solution was available (~ ±0·05 D.), and the hydrocarbons, which are considered separately.

All dipole moments are in Debye units, and all refractions, etc., in c.c.

Results.—These are presented as before (*J.*, 1951, 16). To save space and facilitate cross-referencing, each compound has been allotted an identity number, printed in Clarendon type; the key to the numbering will be found in Tables V and VI. Also, each solution of compounds **15** - **44** has been numbered (key : Table II) to save repeating concentrations in Table III. Derivatives of each hydrocarbon are arranged alphabetically, those of benzene appearing first, then of styrene, then of diphenyl, then of stilbene, and finally of diphenylbutadiene.

TABLE V.

		ε_1'.	α.	v_1'.	$-10^3\beta$.	${}_{\mathrm{T}}P$.	$[R]_{\mathrm{D}}$, calc.	μ.
1	Styrene	2·2726	0·126	1·14494	31	37·0	36·5	$<0·3$
2	4-Acetylstilbene	2·2728	5·396	1·14508	242	285·5	75·8	3·20
3	2-Aminostilbene	2·2727	1·663	1·14497	212	115·4	70·1	1·49
4	3-Aminostilbene	2·2725	1·782	1·14507	263	116·8	70·1	1·51
5	4-Aminostilbene	2·2727	2·833	1·14486	224	157·7	70·1	2·07
6	4-Cyanostilbene	2·2727	10·788	1·14539	261	470·7	71·0	4·42
7	2-Dimethylaminostilbene	2·2729	0·921	1·14502	171	103·5	80·3	1·07
8	3-Dimethylaminostilbene	2·2728	1·773	1·14497	200	137·3	80·3	1·67
9	4-Dimethylamino-2′ : 5′-dimethylstilbene	2·2728	2·697	1·14522	189	199·2	90·1	2·31
10	4-Dimethylamino-2′-ethylstilbene	2·2726	2·964	1·14504	177	212·7	90·1	2·45
11	4-Dimethylamino-2′-methylstilbene	2·2728	3·261	1·14512	184	213·6	85·2	2·51
12	4-Nitrostilbene	2·2727	10·342	1·14498	264	497·5	72·2	4·56
13	1-*p*-Nitrophenyl-4-phenylbuta-1 : 3-diene	2·2724	10·365	1·14498	309	552·6	91·6	4·75

TABLE VI.

		ε_1'.	α.	v_1.	v_1'.	$-10^3\beta$.	$10^3\gamma$.	${}_{\mathrm{T}}P$.	μ.
14	Benzonitrile	2·2728	17·316	1·14462	1·14461	147	32	366·7	4·05
15	*p*-Phenylenediamine	2·2726	2·939	1·14650	1·14653	300	104	87·1	1·60
16	*NNN′N′*-Tetramethyl-*p*-phenylenediamine	2·2727	0·997	1·14609	1·14608	116	66	81·2	1·12
17	4-Bromostyrene	2·2727	1·515	1·14465	1·14465	420	48	91·7	1·52
18	4-Chlorostyrene	2·2728	1·902	1·14471	1·14470	217	60	87·9	1·50
19	4-Dimethylaminostyrene	2·2728	3·698	1·14462	1·14460	126	99	147·0	2·17
20	*β*-Nitrostyrene	2·2724	15·009	1·14655	1·14652	335	97	457·2	4·50
21	4-Nitrostyrene	2·2727	13·196	1·14465	1·14644	283	64	408·6	4·23
22	Benzidine	2·2728	1·943	1·14650	1·14652	302	178	113·6	1·60
23	4-Bromodiphenyl	2·2726	1·512	1·14467	1·14467	432	88	115·9	1·65
24	4-Cyanodiphenyl	2·2725	11·630	1·14470	1·14468	251	104	440·0	4·33
25	4-Dimethylaminodiphenyl	2·2727	2·599	1·14465	1·14461	193	127	152·4	2·04
26	4-Nitrodiphenyl	2·2729	10·936	1·14636	1·14635	347	107	457·3	4·41
27	*NNN′N′*-Tetramethylbenzidine	2·2726	0·998	1·14661	1·14664	215	144	111·7	1·21
28	4-Amino-4′-bromostilbene	2·2728	5·458	1·14650	1·14649	475	180	336·3	3·56
29	4-Bromostilbene	2·2728	1·503	1·14526	1·14526	408	114	130·2	1·67
30	*cis*-4-Bromo-4′-nitrostilbene	2·2724	7·579	—	1·14520	479	108	494·2	4·52
31	*trans*-4-Bromo-4′-nitrostilbene	2·2728	3·792	1·14465	1·14462	479	161	277·3	3·11
32	2-Chloro-4′-dimethylaminostilbene	2·2726	3·353	1·14459	1·14456	280	190	229·0	2·65
33	4-Chloro-4′-dimethylaminostilbene	2·2728	7·216	1·14465	1·14468	290	197	415·6	4·02
34	3-Cyanostilbene	—	9·34	1·14467	—	244	130	416	4·12
35	4-Diethylaminostilbene	2·2728	3·483	1·14465	1·14462	174	181	237·5	2·69
36	4-Dimethylaminostilbene	2·2729	3·220	1·14526	1·14526	193	201	198·6	2·41
37	4-Dimethylamino-2 : 2′-dimethylstilbene	2·2728	2·561	1·14459	1·14457	173	159	193·9	2·25
38	4-Dimethylamino-4′-nitrostilbene	2·2726	22·731	1·14459	1·14459	360	342	1210·4	7·42
39	4-Dimethylamino-2′ : 4′ : 6′-trimethylstilbene	2·2728	2·170	1·14455	1·14459	182	141	184·5	2·11
40	4-Methoxy-4′-nitrostilbene	2·2728	13·309	1·14459	1·14458	341	192	700·5	5·51
41	Stilbene	2·2726	0·394	1·14655	1·14654	194	151	64·4	(0)
42	2 : 4 : 6-Trimethylstilbene	2·2728	0·327	1·14450	1·14452	138	105	80·4	$<0·4$
43	Triphenylethylene	2·2726	0·431	—	1·14516	230	149	90·6	$<0·3$
44	1-*p*-Dimethylaminophenyl-4-phenylbuta-1 : 3-diene	2·2728	3·468	1·14630	1·14631	158	260	236·0	2·58

DISCUSSION.

Table IV gives some values of the exaltations of molar refractions for $\mathrm{Na_D}$ light, expressed as $\mathrm{E}[R]_{\mathrm{D}} = [R]_{\mathrm{D}}$, obs., $-[R]_{\mathrm{D}}$, calc. The calculated values have been obtained, not from atomic refractions as is sometimes done, but from the refraction of the parent hydrocarbon plus a value for each of the substituents; and the latter is taken as the difference between the refractions of the benzene derivative and of benzene itself.

Because atom polarisations (${}_{\mathrm{A}}P$) cannot often be measured, it is often assumed that the error in neglecting them is just balanced by the error arising from failure to extrapolate molar refractions to infinite wave-length in order to obtain the true electron polarisation, ${}_{\mathrm{E}}P$. The second error is equal to the molar dispersion, $\mathbf{D} = [R]_{\mathrm{D}} - [R]_{\infty}$, as it was defined by Bauer and Fajans (*J. Amer. Chem. Soc.*, 1942, **64**, 3023). Some of the exaltations in Table IV are sufficiently large as to suggest that the approximation, ${}_{\mathrm{A}}P$ = **D**, is invalid.

Just as the approximation is unreliable when ${}_{\mathrm{A}}P$ is abnormally large (Coop and Sutton, *J.*, 1938, 1269), so with **D**. It has been suggested (Everard, Hill, and Sutton, *Trans. Faraday Soc.*, 1950, **46**, 417) that the best compromise in these circumstances is to take as the distortion polarisation (${}_{\mathrm{E}}P + {}_{\mathrm{A}}P$) the *calculated* value of $[R]_{\mathrm{D}}$ (as defined above). If this is done, the allowance implicitly made for ${}_{\mathrm{A}}P$ is $[R]_{\mathrm{D}}$ (calc.) $- [R]_{\infty}$. When this quantity is calculated for the 18 compounds in this series for which the necessary data exist, it is found in 15 cases to be 5 ± 2 c.c. (Table IV). This seems a more reasonable estimate of the atom polarisation of such compounds as these than the larger and more variable one of 4—14 c.c. provided by the quantity **D**.

It is important to note that, if calculated $[R]_{\mathrm{D}}$ values are used for distortion polarisations, they should not be based on atomic refractions except for very simple compounds. For example, Angyal and Le Fèvre have given the calculated molar refraction of anthranyl methyl ether (9-methoxyanthracene) as 61·5 c.c. (*J.*, 1950, 562), which is lower than both the observed refraction and the total polarisation of anthracene itself [67 and 67·9 c.c., respectively (Campbell, Le Fèvre, Le Fèvre, and Turner, *J.*, 1938, 404). Steiger, however, gives the former as 65·4 c.c. (see *Ber.*, 1923, **56**, 998, and references therein)]. It should be *ca.* 6 c.c. higher {cf. $[R]_{\mathrm{D}}$ (obs.) for 9 : 10-dimethoxyanthracene, 79·8 c.c.; Everard and Sutton, *J.*, 1951, 16}. The discrepancy arises from the use of atomic refractions, and leads to a dipole moment value 0·2 too high.

Comparison with Previous Work.—In Table VII are given the dipole moments of compounds which have been examined before, under μ (ii), together with the values obtained in the present work, under μ (i), for comparison.

TABLE VII.

Compound.	*μ*. (i.)	*μ*. (ii.) *	References and remarks.†
Styrene	<0·3	0—0·37	" Tables "; von Hippel and Wesson, *Ind. Eng. Chem.*, 1946, **38**, 1121.
4-Bromostyrene	1·52	1·35	Otto and Wenzke, *J. Amer. Chem. Soc.*, 1935, **57**, 294.
4-Chlorostyrene	1·50	1·28	*Idem, ibid.*
β-Nitrostyrene	4·50	4·27,‡ 4·48	Goebel and Wenzke, *ibid.*, 1938, **60**, 697; Bergmann, *J.*, 1936, 402.
Benzonitrile	4·05	3·74—4·02	11 Values in benzene, all ⩾15 years old : " Tables."
p-Phenylenediamine	1·60	0—1·56	Very discordant values : " Tables."
Tetramethyl-*p*-phenylene-diamine	1·12	1·23	Weissberger and Sängewald, *Z. physikal. Chem.*, 1929, *B*, **5**, 237.
Tetramethylbenzidine	1·21	1·25	*Idem, ibid.*
Benzidine	1·60	1·3—1·43	" Tables "; Sahney, Beri, Sarna, and Singh, *J. Ind. Chem. Soc.*, 1949, **26**, 329.
4-Bromodiphenyl	1·65	1·64	Le Fèvre and Le Fèvre, *J.*, 1936, 1130.
4-Nitrodiphenyl	4·41	4·17, 4·28	*Idem, ibid.*; Næshagen, *Z. physikal. Chem.*, 1934, *B*, **25**, 157. The cause of the discrepancy is obscure.
Stilbene	(0)	0	Eide and Hassel, *Tids. Kjemi Berg.*, 1930, **10**, 93; Smyth and Dornte, *J. Amer. Chem. Soc.*, 1931, **53**, 1296.
Triphenylethylene	<0·3	0·6	*Idem, ibid.*
4-Dimethylamino-4′-nitro-stilbene	7·42	8·3 §	Weizmann, *Trans. Faraday Soc.*, 1940, **36**, 978. This value is based on one very dilute solution only.
4-Methoxy-4′-nitrostilbene	5·51	7·8	*Idem, ibid.* An ε–ω plot of the earlier work is much more erratic than that now obtained.

* These measurements were carried out in benzene solution unless otherwise stated.

† The reference " Tables " alludes to Wesson's " Tables of Electric Dipole Moments," Technology Press, 1948.

‡ Measured in dioxan.

§ Measured in 1-methylnaphthalene.

The Choice of Dipole Moment Values from the Literature.—In this series of papers it has been necessary to select a considerable number of dipole moment values from the literature. Examination of any tables of dipole moments (*e.g.*, Wesson, *op. cit.*, Technology Press, 1948) reveals a most troublesome degree of disagreement between the measurements of different investigators; and until recently, few attempts have been made to elucidate the causes of disagreement. Some of the discrepancies are, of course, due to solvent effects, but they often occur even between measurements with the same solvent at the same temperature. The chief causes (apart from the use of impure materials and unsuitable technique or apparatus) are the computation of polarisations at infinite dilution by unreliable methods [the importance of this has recently been stressed by Everard, Hill, and Sutton (*Trans. Faraday Soc.*, 1950, **46**, 417), *inter al.*], the different allowances made by different investigators for atom polarisation, and the use of values of the universal constants N and k which have since been revised.*

Discrepancies due to these three causes, which are to be especially suspected in early work, can always be corrected *a posteriori*, provided that experimental details are published. Recalculation is arduous, however, and has been attempted only on a very limited scale (*e.g.*, by Halverstadt and Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988, and by Smith and Cleverdon, *Trans. Faraday Soc.*, 1949, **45**, 109). Consequently, no *critical* tables of dipole moments exist, and users of ordinary tables are obliged to exercise personal judgment or else to re-examine compounds themselves.

We give the following general rules as a guide, though fortunately they do not always apply : (i) Certain moments in solution have been given to as many as four decimal places; the third and the fourth should be ignored. (ii) Moments >1 required accurate to $<\pm 0{\cdot}1$ should be recalculated (if previously obtained from the extrapolation of polarisation–concentration graphs); those <1 required accurate to $<\pm 0{\cdot}1$, and those >1 required accurate to $<\pm 0{\cdot}05$ should be remeasured with suitable precautions. (iii) Moments $<0{\cdot}4$ are indistinguishable from zero.

TABLE VIII.

Dipole moments in benzene solution at 25°.

Group :	NO_2.	Ac.	CN.	NH_2.	NMe_2.	Br.	Cl.	F.	I.	Me.
Alkyl derivative	3·25	2·75	3·60	1·32	0·86	2·00	2·01	1·89	1·92	0
Range of uncertainty...	3·1—3·3	±0·05	3·5—3·65	±0·05	?	±0·1	±0·1	?	±0·1	—
No. of vals. published [a]	4	25	7	9	1	22	14	2	16	—
Phenyl derivative	4·01 [b]	2·96 [c]	4·05 [d]	1·52 [e]	1·61 [f]	1·57 [g]	1·60 [h]	1·48 [i]	1·42 [j]	0·35 [k]
Range of uncertainty...	3·98—4·02	±0·02	±0·01	±0·01	±0·01	±0·02	±0·01	±0·01	±0·01	±0·05

[a] Sources : Wesson, *op. cit.*; Few and Smith, *J.*, 1949, 2663; Barclay, Le Fèvre, and Smythe, *Trans. Faraday Soc.*, 1951, **47**, 357. [b] Nitrobenzene has been the subject of a detailed investigation by Smith and Cleverdon (*Trans. Faraday Soc.*, 1949, **45**, 109), who, however, make a large allowance for atom polarisation. We take their value for ${}_{\mathrm{T}}P$, but put ${}_{\mathrm{D}}P = [R]_{\mathrm{D}}$. Le Fèvre (*ibid.*, 1950, **46**, 1) has measured no fewer than 111 solutions, divided into three sets, but fails to get internal consistency (${}_{\mathrm{T}}P$ values of 354·8, 356·1, and 358·6 c.c.). [c] Bentley, Everard, Marsden, and Sutton, *J.*, 1949, 2957. Le Fèvre and Le Fèvre give 2·89 (*J.*, 1950, 1829), but this value is clearly a mistake for 2·97 (confirmed by personal communication). [d] Present work. [e] Le Fèvre, Roberts, and Smythe have measured 13 solutions, giving $\mu = 1{\cdot}51_7$ (*J.*, 1949, 902), and Few and Smith, 16 solutions, giving $\mu = 1{\cdot}52_7$ (*ibid.*, p. 753); recalculated. [f] Few and Smith (*ibid.*); Marsden and Sutton (*J.*, 1936, 599); recalculated. Barclay, Le Fèvre, and Smythe (*loc. cit.*). [g] Otto and Wenzke (*Ind. Eng. Chem. Anal.*, 1934, **6**, 187) and Le Fèvre and Le Fèvre (*J.*, 1936, 1130); recalculated. Brown and De Vries (*J. Amer. Chem. Soc.*, 1951, **73**, 1811). [h] Le Fèvre (*loc. cit.*) (45 solutions); Curran (*J. Amer. Chem. Soc.*, 1942, **64**, 830) and Spinrad (*ibid.*, 1946, **68**, 617); recalculated. Brown and De Vries (*loc. cit.*). [i] Leonard and Sutton (*ibid.*, 1948, **70**, 1564) give 1·46 (1·48, recalculated), the value 1·53 given in this paper being a misprint for 1·43; Freiser, Hobbs, and Gross (*ibid.*, 1949, **71**, 111) give 1·47. Le Fèvre and Le Fèvre give 1·48 (recalculated), and Brown and De Vries, 1·50 (*locc. cit.*). [j] Saxby, personal communication. This value differs markedly from previous ones. [k] This value, being small, is difficult to fix with certainty. Le Fèvre, Le Fèvre, and Robertson give 0·34, but no details (*J.*, 1935, 480). Dielectric-loss measurements give 0·30—0·32 (Whiffen and Thompson, and Cripwell and Sutherland, *Faraday Soc. Discussion* on " Dielectrics," 1946, pp. 114, 122, 149). Vapour-phase measurements (probably comparable in this case) give 0·35 (McAlpine and Smyth, *J. Amer. Chem. Soc.*, 1933, **55**, 453) and 0·37 (Baker and Groves, *J.*, 1939, 1144).

Further information about the reliability of a measurement can be obtained by plotting a dielectric constant–concentration graph, and seeing whether it extrapolates to the ε_1 value which the authors give; if not, unless Halverstadt and Kumler's method of computation (*loc. cit.*) had been used, the moment quoted is likely to be unreliable. Also, except for highly polar compounds, a marked (apparent) dependence of polarisation on concentration is usually indicative of error.

All dipole-moment values taken from the literature and cited in this series of papers have been recalculated, where possible and useful, from the experimental observations on which

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* We take $N = 6{\cdot}0226 \times 10^{23}$ mole^{-1} and $k = 1{\cdot}3806$ erg deg.$^{-1}$ (Kaye and Laby, " Physical and Chemical Constants," Longmans, Green & Co., 10th edn., 1948), giving $\mu = 0{\cdot}2212\sqrt{{}_{\mathrm{O}}P}$ at 25°; the latest revision (Bearden and Watts, *Physical Rev.*, 1951, **81**, 73) does not alter this.

they were based, the same assumptions being used about $\boldsymbol{N}$, $\boldsymbol{k}$, and ${}_{D}P$ as have been made in treating the measurements reported in this paper for the first time.

It is convenient to collect together some of these values which are used in Parts II—VI, *viz.*, those which refer to monosubstituted derivatives of paraffin hydrocarbons and of benzene (Table VIII). The former set does not refer to the derivatives of any particular paraffin, because it is needed in the estimation of mesomeric moments; so greater weight has been attached, when practicable, to observations on compounds with large groups, which might be expected to have much the same electrostatic polarisability as a benzene ring.

Dipole Moments of Stilbene, 2 : 4 : 6-*Trimethylstilbene, Triphenylethylene, and Styrene*—The total polarisation of stilbene is 64·4 ± 0·5; $[R]_D$ exceeds this by 1·4; and $[R]_\infty$ is 61·4 ± 0·5. It is clear that **D** exceeds ${}_{A}P$. The atom polarisation of a molecule such as this may be estimated additively (Coop and Sutton, *J.*, 1938, 1269; Audsley and Goss, *J.*, 1941, 864). That of ethylene is 0·4 (Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144), and that of benzene is 1·5 [from ${}_{T}P$ and $[R]_\infty$ of liquid. However, Groves and Sugden give 1·1 (*J.*, 1934, 1094), and Cartwright and Errera, 0·55 (*Acta Physicochim. U.R.S.S.*, 1935, **3**, 649)]. Hence, that of stilbene should be *ca.* 3·4. As ${}_{T}P - [R]_\infty$ is 3·0, ${}_{O}P$ is evidently very near to zero. Such non-polarity is, of course, in accordance with the symmetrical nature of the molecule as shown by *X*-ray examination (Robertson and Woodward, *Proc. Roy. Soc.*, 1937, *A*, **162**, 568).

In contrast, the total polarisations of 2 : 4 : 6-trimethylstilbene (80·4 ± 1) and of triphenyl ethylene (90·6 ± 0·8) are not less than their $[R]_D$ (obs.) values (78·7 and 90·6, respectively): their $[R]_\infty$ values are 75·0 ± 1 and 85·0 ± 1, so the values of ${}_{T}P - [R]_\infty$ are 5·4 and 5·6. Calculated atom polarisations are 3·7 and 4·9 (each methyl group is regarded as contributing 0·1: Audsley and Goss, *loc. cit.*). It is therefore possible that these two unsymmetrical molecules may be slightly polar (moments of $\ngtr 0{\cdot}4$ and $\ngtr 0{\cdot}3$, respectively).

The exaltation of 2 : 4 : 6-trimethylstilbene is 1·3 less than that of stilbene, which indicates that there is less conjugation. That of triphenylethylene is about the same, suggesting that the introduction of an extra phenyl group does not here increase the conjugation. These two facts can be readily ascribed to steric influences which would cause the systems to be non-coplanar (cf. Part II).

The total polarisation of styrene is 37·0 ± 0·3. Extrapolation of the molar refractions given in Landolt–Börnstein's "Tabellen" yields the value 34·5 for $[R]_\infty$. The calculated atom polarisation is 1·9; whence the moment is 0·17, though unavoidable uncertainties make any value up to 0·3 possible. Von Hippel and Wesson obtain the value of 0·12 ± 0·03 by the dielectric-loss method (*Ind. Eng. Chem.*, 1946, **38**, 1121); this value is probably more reliable than any obtainable in the orthodox manner (see, however, Heston and Smyth, *J. Amer. Chem. Soc.*, 1950, **72**, 99, and Whiffen, *Trans. Faraday Soc.*, 1950, **46**, 124, for a possible complication). Torkington has concluded from the infra-red spectrum of styrene that "there is a resultant negative charge on the terminal carbon atom of the vinyl group . . . which will be associated with *meta*-substitution in the phenyl nucleus" (*Nature*, 1949, **163**, 179). An indirect argument that styrene has a moment of *ca.* 0·12 (vinyl group negative) is given in Part IV. The balance of evidence, then, is that styrene is a slightly polar molecule.

This result is of considerable theoretical interest, because, according to simple molecular-orbital theory, alternant hydrocarbons (such as the above) should be non-polar (Coulson and Rushbrooke, *Proc. Camb. Phil. Soc.*, 1940, **36**, 193). However, Laforgue (*J. Chim. physique*, 1951, **48**, 17) has very recently refined the earlier calculations by applying ten different kinds of correction, and has obtained a moment of 0·15 for styrene, the vinyl group being negative. The agreement with the experimental value is very satisfactory, though it should be remembered that the range of uncertainty in each is large.

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[*Received, May* 15*th*, 1951.]