cis–trans Equilibrium in *meta*-Chlorophenyl Aldehydes, Ethers, Ketones, and Carboxylic Esters from Dipole Moment Studies

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Comparison of dipole moments of *meta*-chloro-, *para*-chloro-, and 3,5-dichloro-substituted compounds with parents enable the calculation of group dipole directions, of interaction moments, and of *cis–trans* conformational equilibria in the *meta*-substituted derivatives.

THE use of dipole moment measurements in conformational analysis [1] requires knowledge of the group moment directions in addition to magnitudes. Previously, such directions for substituents attached to a benzene ring have been determined from comparison of parent and *para*-substituted derivatives,[2,3] but this presupposes no interaction between the groups, which is incorrect. In connection with other work [4] we required *cis–trans* equilibrium constants for *meta*-susbstituted benzaldehydes, anisoles, *etc.* To find reliable directions we have now examined a series of 3,5-dichloro-derivatives in which interaction should be minimal; for a previous application of this method see ref. 5.

EXPERIMENTAL

The compounds used, except for the methyl benzoates, were commercially available. They were purified by recrystallisation or redistillation and for each compound impurities were shown to be less than 0·2% by g.l.c. The methyl esters of chlorobenzoic acids were prepared by the usual method from methyl alcohol and the corresponding (commercially available) acid in the presence of concentrated sulphuric acid.

[1] *Cf.* Our series 'Conformational Analysis of Saturated Heterocycles,' M. J. Cook, A. R. Katritzky, and M. Moreno Manas, *J. Chem. Soc.* (*B*), 1971, 1330 and previous papers in this series.

[2] M. J. Aroney, R. J. W. Le Fèvre, R. K. Pierens, and M. G. N. The, *J. Chem. Soc.* (*B*), 1969, 666.

[3] R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 1936, 599.

[4] M. V. Sinnott, Ph.D. Thesis, University of East Anglia, Norwich, 1969.

[5] R. A. Y. Jones, A. R. Katritzky, P. G. Lehman, K. A. F. Record, and B. B. Shapiro, *J. Chem. Soc.* (*B*), 1971, 1302.

Benzene, cyclohexane, and 1,4-dioxan were dried by refluxing over metallic sodium and distilling.

Electric dipole moments were measured by the method previously described.[5] Experimental results are given in Table 1 and calculated values of dipole moments and

TABLE 1

Dielectric and specific volume measurements at 25° [a]

10^6w	$10^6(\varepsilon_{12} - \varepsilon_1)$	$10^6(v_1 - v_{12})$
Chlorobenzene (B)		
4831	11,940	1394
5357	13,250	1426
7544	18,550	1896
7610	19,654	1760
8763	21,903	2090
9600	23,885	2182
9655	23,856	2312
Chlorobenzene (C)		
2704	5712	
5061		2063
7953	16,817	3286
9285	19,586	3782
Chlorobenzene (D)		
3043	9340	200
4909	15,119	
7914	24,400	507
m-Dichlorobenzene (C)		
4081	6325	2030
7518	11,539	3659
11,944	18,408	5871
m-Dichlorobenzene (D)		
3295	7257	595
3949	8881	739
8248	18,077	1488
3-Chlorotoluene (B)		
3924	11,119	666
4060	11,477	460
5208	14,555	851
6212	17,461	1171
10,485	29,361	1711
10,491	29,273	2106
12,667	35,495	2514
3,5-Dichlorotoluene (B)		
4513	11,525	1405
4782		1672
6438	16,142	2261
9461	23,791	3039
3-Chloronitrobenzene (B)		
1399	11,754	571
2487	20,699	1060
2611	21,892	1166
3367	28,134	1421
3416	28,461	1433
3,5-Dichloronitrobenzene (B)		
3368		1641
5187	19,216	2605
7321	26,453	3720
8980	32,219	4756
9346	34,504	
3-Chlorobenzonitrile (B)		
1809	17,376	594
2214	21,257	800
2215	20,791	
2467	27,800	882
2584	24,516	1001
2806	26,415	1003
3234	30,554	1087
3366	31,976	974
3647	34,819	1109

TABLE 1 (*Continued*)

10^6w	$10^6(\varepsilon_{12} - \varepsilon_1)$	$10^6(v_1 - v_{12})$
3,5-Dichlorobenzonitrile (B)		
1417		318
2401	9848	
3642	14,925	1534
3797	15,678	1443
5355	21,711	2064
Methyl benzoate (B)		
2497	7143	554
3131	9089	854
4448	12,778	968
6752	19,587	1264
7214	20,954	1591
8717		1971
9828	28,565	2274
Methyl benzoate (C)		
2605	6128	
4073	9596	1316
5515	12,944	1802
7931	18,706	2580
8722	20,563	2848
10,314	24,320	3431
Methyl benzoate (D)		
2997	10,218	152
3705	12,768	140
4678	16,400	188
7001	24,101	
7984		293
Methyl 3-chlorobenzoate (B)		
2964	7795	1090
7361	19,365	2385
8135	21,313	2778
9793	25,765	3191
13,781	36,298	
Methyl 3-chlorobenzoate (C)		
3455		1605
5756	13,215	2662
9570	22,034	4360
14,395	33,244	
Methyl 3-chlorobenzoate (D)		
2585	8734	710
4027	13,742	630
7180	24,426	1119
7803	26,477	
Methyl 4-chlorobenzoate (B)		
3864	8668	1219
5174	11,739	1675
9012	20,743	3012
13,785	31,747	4378
Methyl 4-chlorobenzoate (C)		
5622	10,917	
6057	11,853	2726
7763	15,139	3465
Methyl 4-chlorobenzoate (D)		
3392	9488	528
4259	12,027	654
6073	16,678	912
8403	23,671	1278
Methyl 3,5-dichlorobenzoate (B)		
3313	6705	1471
5367	10,546	2268
8447	16,649	3551
8734	17,201	3496
9695	19,010	3883
Methyl 3,5-dichlorobenzoate (C)		
3481	5811	1754
4451	7402	2257
5393	9004	2759

TABLE 1 (*Continued*)

10^6w	$10^6(\varepsilon_{12} - \varepsilon_1)$	$10^6(v_1 - v_{12})$
Methyl 3,5-dichlorobenzoate (D)		
2061	4984	453
3344	8045	762
4875	11,720	1066
6250	15,082	1397
Benzaldehyde (B)		
1513	14,084	298
2664	24,849	561
2762	25,774	538
3779	35,197	732
Benzaldehyde (C)		
3503	25,969	
3557	27,072	1042
6345	47,370	1920
9727	72,758	2852
3-Chlorobenzaldehyde (B)		
2791	15,123	882
3843	20,945	1256
4738	25,768	1536
3-Chlorobenzaldehyde (C)		
2958	13,738	1307
5347	24,990	2353
5957	27,655	2653
4-Chlorobenzaldehyde (B)		
2091	5902	556
3738	10,891	1047
4844	15,227	1514
5779	17,484	1618
10,984	34,689	3550
3,5-Dichlorobenzaldehyde (B)		
1267	2956	530
2096	5122	938
3697	8893	1544
4508	10,872	1921
3,5-Dichlorobenzaldehyde (C)		
407	481	175
1482	2607	787
2825	5255	1458
4447	8523	2308
5314	10,195	2783
Acetophenone (B)		
1291	10,170	1626
1985	15,585	3165
4432	34,722	7529
3-Chloroacetophenone (B)		
1842		566
3221	17,309	992
4040	21,806	1245
7171	38,441	2230
4-Chloroacetophenone (B)		
3228	13,021	1347
3821	15,269	1630
5175	20,641	2176
6615	26,408	2769
Anisole (B)		
2757	4455	386
4559	7392	
7507	12,266	1005
7669	12,453	1078
3-Chloroanisole (B)		
1837	6091	550
3155	10,257	880
3813	12,444	1093
3919		1187
4016	12,923	1176
5201	17,069	
6835	22,388	2074
8026	25,962	2366

TABLE 1 (*Continued*)

10^6w	$10^6(\varepsilon_{12} - \varepsilon_1)$	$10^6(v_1 - v_{12})$
4-Chloroanisole (B)		
2865	11,756	861
3745	15,339	1063
4274	17,505	1290
7630	31,128	2240
Styrene (B)		
12,310	1728	361
17,468	2311	564
21,435	2863	686
28,794	4291	912
3-Chlorostyrene (B)		
4202	8779	902
8965	18,738	1951
10,566	22,206	2301
13,777		2965
4-Chlorostyrene (B)		
3596	6786	718
4404	8471	935
7462	14,344	1620
10,744	20,779	2283

Solvents are indicated thus: (B) benzene, (C) cyclohexane, (D) dioxan

standard (random) errors from least squares calculations are given in Table 2.

RESULTS AND DISCUSSION

Symmetrical Substituents.—The compounds with symmetrical substituents were examined primarily to test the accuracy of the method and the assumptions made. Results are collected in Table 3, in which the calculated moments were obtained by vector addition of the individual moments of Table 2. The value for the dipole moment of *m*-dichlorobenzene was used as the group moment for a 3,5-dichlorophenyl group. Comparison of the experimental and calculated dipole moments allows estimation of the accuracy of the method as *ca.* 0·05 D.

Unsymmetrical Substituents: Dipole Directions.—Assuming regular geometry of the benzene ring, the angle θ to the C–X bond at which the group moment Ar–X acts can be calculated from equation (1) where $\mu_{3,5}$ is the moment of the 3,5-dichloro-compound, and $\mu_{m\text{-Cl}}$ is the 3,5-dichlorophenyl group moment, and μ_x the moment of the parent. Values of θ are given in Table 4. The differences between the angle values in the various solvents are not significant.

Using these angles it is possible to calculate the moment expected for the *p*-chloro-compounds on the assumption that there is no electronic interaction between the substituents; the differences between such calculated values and those observed provide a measure of the interaction between the substituents and are tabulated in Table 4. In all cases the interaction is small, being scarcely larger than the experimental error except for *p*-chlorobenzaldehyde. 3,5-Dichloroacetophenone and 3,5-dichlorostyrene were unavailable so the dipole angles for the acetyl and vinyl groups were calculated from the *p*-chloro-compounds on the assumption that the interaction moments here would also be

TABLE 2

Dipole moments at 25° [a]

Compounds	α	$\Delta\alpha$	$-\beta$	$\Delta\beta$	${}_{T}P_{2\infty}$	$\Delta_{T}P_{2\infty}$	${}_{E}P$ [b]	μ	$\Delta\mu$
Measured in benzene:									
Chlorobenzene	2·49	0·04	0·23	0·01	83·6	0·9	29·9	1·62	0·01
m-Dichlorobenzene								1·54 [c]	0·01 [c]
3-Chlorotoluene	2·79	0·01	0·20	0·02	102·0	0·6	34·4	1·82	0·01
3,5-Dichlorotoluene	2·51	0·02	0·33	0·02	115·3	1·0	39·1	1·93	0·01
3-Chloronitrobenzene	8·34	0·03	0·43	0·01	280·7	0·9	37·3	3·45	0·01
3,5-Dichloronitrobenzene	3·64	0·06	0·50	0·01	168·0	2·2	42·0	2·48	0·02
3-Chlorobenzonitrile	9·49	0·07	0·31	0·03	279·6	2·2	34·2	3·47	0·02
3,5-Dichlorobenzonitrile	4·07	0·03	0·41	0·03	169·5	1·8	38·9	2·53	0·02
Methyl benzoate	2·91	0·01	0·22	0·01	112·0	0·6	34·9	1·94	0·01
Methyl 3-chlorobenzoate	2·63	0·00	0·33	0·01	126·1	0·5	39·6	2·06	0·01
Methyl 4-chlorobenzoate	2·30	0·01	0·32	0·01	115·5	0·5	39·6	1·93	0·01
Methyl 3,5-dichlorobenzoate	1·96	0·01	0·40	0·01	121·1	0·8	45·3	1·93	0·01
Benzaldehyde	9·33	0·01	0·20	0·00	216·1	0·3	29·6	3·02	0·00
3-Chlorobenzaldehyde	5·44	0·01	0·33	0·01	178·1	0·4	34·4	2·65	0·00
4-Chlorobenzaldehyde	3·24	0·05	0·34	0·01	119·5	1·5	34·4	2·04	0·02
3,5-Dichlorobenzaldehyde	2·42	0·02	0·42	0·01	117·1	0·8	39·1	1·95	0·01
Acetophenone	7·83	0·01	0·17	0·01	211·6	0·4	34·3	2·95	0·00
3-Chloroacetophenone	5·39	0·01	0·31	0·00	195·0	0·3	39·0	2·76	0·00
4-Chloroacetophenone	3·99	0·01	0·20	0·00	149·3	0·4	39·0	2·32	0·01
Anisole	1·63	0·01	0·14	0·00	65·7	0·1	31·4	1·30	0·00
3-Chloroanisole	3·25	0·02	0·30	0·01	122·9	0·5	36·1	2·06	0·00
4-Chloroanisole	4·08	0·01	0·29	0·01	145·5	0·3	36·1	2·31	0·00
3,5-Dichloroanisole								2·26 [c]	0·02 [c]
Styrene	0·15	0·01	0·03	0·00	37·4	0·2	33·6	0·43	0·01
3-Chlorostyrene	2·10	0·01	0·22	0·00	93·1	0·2	38·3	1·64	0·00
4-Chlorostyrene	1·94	0·01	0·22	0·00	88·9	0·3	38·3	1·57	0·01
Measured in cyclohexane:									
Chlorobenzene	2·11	0·00	0·41	0·00	82·2	0·1	29·9	1·60	0·00
m-Dichlorobenzene	1·54	0·01	0·43	0·00	84·2	0·2	34·6	1·56	0·00
Methyl benzoate	2·36	0·00	0·33	0·00	110·2	0·2	34·9	1·92	0·00
Methyl 3-chlorobenzoate	2·30	0·00	0·46	0·00	130·5	0·4	39·6	2·11	0·01
Methyl 4-chlorobenzoate	1·95	0·01	0·45	0·00	116·4	0·4	39·6	1·94	0·00
Methyl 3,5-dichlorobenzoate	1·67	0·00	0·51	0·00	122·7	0·3	45·3	1·95	0·00
Benzaldehyde	7·47	0·04	0·30	0·01	217·4	1·1	29·6	3·03	0·01
3-Chlorobenzaldehyde	4·66	0·02	0·44	0·00	187·5	0·7	34·4	2·74	0·01
3,5-Dichlorobenzaldehyde	1·98	0·01	0·52	0·00	117·4	0·3	39·1	1·96	0·00
Measured in 1,4-dioxan:									
Chlorobenzene	3·08	0·00	0·06	0·00	86·7	0·1	29·9	1·67	0·00
m-Dichlorobenzene	2·19	0·02	0·18	0·00	86·7	0·6	34·6	1·60	0·01
Methyl benzoate	3·46	0·03	0·04	0·00	114·3	0·8	34·9	1·97	0·01
Methyl 3-chlorobenzoate	3·40	0·01	0·16	0·00	135·7	0·2	39·6	2·17	0·00
Methyl 4-chlorobenzoate	2·80	0·03	0·15	0·00	119·1	1·0	39·6	1·97	0·01
Methyl 3,5-dichlorobenzoate	2·41	0·01	0·22	0·00	125·8	0·3	45·3	1·98	0·00

[a] $\alpha = d\varepsilon/dw$; $\beta = dv/dw$ Standard deviations indicated by Δ. [b] Calculated from bond electronic polarisations; R. J. W. Le Fèvre and K. D. Steel, *Chem. and Ind.*, 1961, 670. [c] From R. A. Y. Jones, A. R. Katritzky, B. B. Shapiro, M. S. Tute, B. Gadsby, and R. W. Broadbent, *J. Chem. Soc.* (*B*), 1971, 1325.

small. The results for these two systems must be considered somewhat less accurate than the others.

$$\mu^2_{3,5} = \mu^2_{m\text{-Cl}} + \mu^2_{X} - 2\mu_{m\text{-Cl}}\,\mu_{X}\cos\theta \quad (1)$$

$$N_{cis} = \frac{\mu^2_{meta} - \mu^2_{trans}}{\mu^2_{cis} - \mu^2_{trans}} \quad (2)$$

$$\mu^2_{trans} = \mu^2_{X} + \mu^2_{Cl} + 2\mu_{X}\mu_{Cl}\cos(120 + \theta) \quad (3)$$

$$\mu^2_{cis} = \mu^2_{X} + \mu^2_{Cl} + 2\mu_{X}\mu_{Cl}\cos(120 - \theta) \quad (4)$$

$$N_{cis} = \frac{\mu^2_{meta} - \mu^2_{X} - \mu^2_{Cl} - 2\mu_{X}\mu_{Cl}\cos(120 + \theta)}{3{\cdot}464\mu_{X}\mu_{Cl}\sin\theta} \quad (5)$$

$$\Delta E = E_{cis} - E_{trans} = \frac{2\mu_{X}\mu_{Cl}\sin\theta}{\varepsilon kT}\left(\frac{\sin\alpha_1}{R_1^2} - \frac{\sin\alpha_2}{R_2^2}\right) \quad (6)$$

Unsymmetrical Substituents: cis–trans *Equilibria.*—The fraction N_{cis} of the *cis*-form in the equilibria of which [(1) ⇌ (2)] is an example, are given in equation (2), in which μ_{meta} is the observed moment of the *m*-chloro-compound and where μ_{trans} and μ_{cis} can be calculated by assuming the ring and substituent to be coplanar using equations (3) and (4); μ_{Cl} is the observed

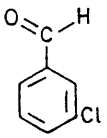
TABLE 3

Comparison of observed and calculated moments (D) at 25° in benzene for compounds with symmetrical substituents

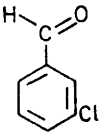
Parent compound	Group [a] moment	3-Chloro		3,5-Dichloro	
		Obs.	Calc.	Obs.	Calc.
Toluene	0·43	1·82	1·87	1·93	1·97
Nitrobenzene	3·95	3·45	3·44	2·48	2·41
Benzonitrile	3·95	3·465	3·44	2·53	2·41

[a] Calculated from data given by A. L. McClellan, 'Tables of Experimental Dipole Moments,' W. H. Freeman, San Francisco–London, 1963.

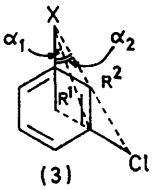
moment of chlorobenzene. Substituting and simplifying give (5). Values of N_{cis} are recorded in Table 4.



(1) (*trans*)



(2) (*cis*)



(3)

In all compounds except for the styrenes (in which the equilibrium constant is approximately unity) the *trans*-conformer, in which the repulsion between dipoles of the chloro group and the other substituent is minimised, is predominates. Further the greater the dipole of the substituent the greater is the extent of this predominance. We have endeavoured to calculate the magnitude of the dipolar repulsions using equation (6) in which E is the repulsion energy between the two dipoles, and the angles α and distances R are as illustrated in (3); that is, we assume point charges at the carbon and chlorine atoms for the C–Cl dipole, but a point dipole acting at the sp^2 carbon atoms of the carbonyl substituents, at the α-carbon atom in styrene, or at the oxygen atom of anisole. Bond lengths used in determining R and α were: C–C (ring), 1·39; C–Cl, 1·70; C_{aryl}–C_{subst}, 1·50; C–O (in anisoles), 1·38. The difficulty with these calculations is always in selecting an appropriate value for ε, the dielectric constant for the 'medium' between the interacting dipoles. For many years a value of 2 was generally recommended [6]; current opinion,[7] which we have followed, favours a value of 1. The results of these calculations, expressed in terms of N_{cis}, are included in Table 4 for comparison with the experimental values. The agreement is in all cases reasonable and in some cases very good, despite the uncertainties in the calculations. In particular: (i) because of induced polarisation the moments calculated by vector addition will not be strictly accurate even when the substituents are *meta* to each other (the dipole moment of *m*-dichlorobenzene is less than that calculated from two chlorobenzene moments by 0·8 D). (ii) The influence of solvent on the polarisability of the solute is incalculable; the results obtained for the relatively inert solvent cyclohexane are the most reliable. (iii) The calculations of electrostatic repulsions are likely to be in error both because of the assumption that the substituents behave as point dipoles at the α-atom and because of the unreliability of the microscopic dielectric constant.

TABLE 4

Unsymmetrical substituents: dipole directions, *cis–trans*-equilibria in *meta*-chloro-derivatives and interaction moments in *para*-chloro-derivatives

Substituent	Solvent [a]	Direction θ (°) [b]	*cis*-Conformer [c]		*trans*-Conformer [c]	Interaction moment [d]
			Population % (N_{cis} × 100)			
			μ_{calc}	Found	Calc.	μ_{calc}	$\mu_{exp} - \mu_{calc}$
OMe	B	105·4	2·893	41·2	41·3	1·165	−0·015
CO_2Me	B	66·0	3·18	41·1	43·8	0·370	−0·03
CO_2Me	C	67·1	3·10	43·7	43·9	0·392	−0·025
CO_2Me	D	66·6	3·25	43·7	43·5	0·369	−0·041
−CHO	C	34·6	3·54	47·3	44·1	1·727	—
−CHO	B	34·4	3·54	42·8	44·0	1·708	+0·125
−Ac [e]	B	51·8	3·85	44·5	42·0	1·360	—
$-CH{:}CH_2$ [e]	B	75·8	1·95	51·5	48·5	1·21	—

[a] B = Benzene, C = cyclohexane, D = dioxan. [b] Direction of moment in monosubstituted benzene relative to C-substituent bond, calculated from 3,5-dichloro-compounds. [c] In *m*-chloro-compounds. [d] In *p*-chloro-compounds. [e] Calculated from *p*-chloro-compounds.

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