Molecular Polarisability. The Conformations of 1-Acetyl- and 1,5-Diacetyl-naphthalenes and -anthracenes

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Dipole moments and molar Kerr constants ($\times 10^{12}$) at 25° are reported for the following as solutes in carbon tetrachloride: 1-chloroanthracene (1·43 D, +229), 1-cyanoanthracene (4·14 D, +870), 1-acetylnaphthalene (2·89 D, +203), 1-acetylanthracene (2·67 D, +243), 1,5-diacetylnaphthalene (2·13 D, −379), and 1,5-diacetylanthracene (2·13 D, −500). For 1-acetylnaphthalene and 1-acetylanthracene, the experimental results are consistent with effective conformational angles of 46 and 42°, respectively, between the C–CO–C plane and the plane of the aromatic ring. The two diacetyl compounds have been considered as mixtures of *cis*- and *trans*-conformations in which the C–CO–C planes are inclined at 45° to the aromatic plane.

INFORMATION concerning the preferred molecular conformations of 1-acetylnaphthalene, 1-acetylanthracene, 1,5-diacetylnaphthalene, and 1,5-diacetylanthracene has been obtained through measurements of the dipole moments and molar Kerr constants of these compounds as solutes in carbon tetrachloride at 25°. In order to determine the polarisabilities of the 1-anthryl group we have also examined 1-chloroanthracene and 1-cyanoanthracene. Observations and results are recorded and discussed below.

EXPERIMENTAL

Solutes.—1-Acetylnaphthalene, as obtained by the best literature method,[1] contained 8% of the 2-isomer (g.l.c.). It was purified by conversion to the picrate, regeneration on a column of alumina, and distillation (b.p. *ca.* 115°/0·2 mm.). 1,5-Diacetylnaphthalene, m.p. 133°, was obtained by the prolonged action of an excess of acetyl chloride and aluminium chloride on naphthalene in boiling carbon disulphide.[2] 1-Acetylanthracene, m.p. 110·5—111°, and 1,5-diacetylanthracene, m.p. 223·5—224°, were prepared and purified as described earlier.[3] 1-Chloroanthracene[4] was chromatographed on alumina from benzene solution, the eluate filtered through charcoal, the solvent evaporated, and the residue purified by crystallisation from alcohol, and glacial acetic acid; m.p. 81·5° (Found: C, 78·75; H, 3·1; Cl, 16·9. Calc. for $C_{14}H_9Cl$: C, 79·1; H, 4·25; Cl, 16·75%). 1-Cyanoanthracene[4] was chromatographed on a long column of alumina, the final fraction being pure, m.p. 141·5—142° (the m.p. is particularly sensitive to small amounts of impurities). All compounds were chromatographically pure (g.l.c. or t.l.c.).

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[1] G. Baddeley, *J. Chem. Soc.*, **1949**, S99.

[2] P. H. Gore and C. K. Thadani, unpublished.

[3] P. H. Gore and C. K. Thadani, *J. Chem. Soc.* (*C*), **1966**, 1729.

[4] P. H. Gore, *J. Chem. Soc.*, **1959**, 1616.

Solvents.—Carbon tetrachloride was fractionated and dried ($CaCl_2$); benzene was fractionally crystallised, distilled, and dried over sodium. The following data apply at 25°:

	ε_1	d_1	$(n_1)_D$	10^7B_1
Carbon tetrachloride ...	2·2270	1·58454	1·4575	0·070
Benzene	2·2725	0·87378	1·4973	0·410

Apparatus.—Dielectric constants were determined with apparatus as in ref. 5; associated procedures to give polarisations were standard.[6a] Kerr effects at 589 nm. were recorded photometrically.[7]

TABLE 1

Incremental dielectric constants, densities, refractive indices, and Kerr effects for solutions at 25°

1-Chloroanthracene in carbon tetrachloride

10^6w_2	1833	2656	3668	4888	6057	14,872
$10^4\Delta\varepsilon$	53	81	116	145	192	448
$-10^5\Delta d$	70	107	155	199	246	
$10^4\Delta n$	7	10	14	18	23	
10^6w_2	1771	2801	3439	4431	5092	14,872
$10^{11}\Delta B$	185	282	347	445	512	1497

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 3{\cdot}05$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}407$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}377$; $\Sigma\Delta n^2/\Sigma w_2 = 1{\cdot}099$; $10^7\Sigma\Delta B/\Sigma w_2 = 10{\cdot}09$

1-Cyanoanthracene in carbon tetrachloride

10^6w_2	960	1482	1506	1862	2287	2785
$10^4\Delta\varepsilon$	172	262	268	325	404	482
$-10^5\Delta d$	58	84	97	109	124	153
$10^4\Delta n$	5	7	7	9	10	13
$10^{11}\Delta B$	387	602	605	751	931	1136

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 17{\cdot}58$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}574$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}469$; $\Sigma\Delta n^2/\Sigma w_2 = 1{\cdot}360$; $10^7\Sigma\Delta B/\Sigma w_2 = 40{\cdot}5$

1-Acetylnaphthalene in carbon tetrachloride

10^5w_2	304	454	814	876
$10^{11}\Delta B$	347	517	925	1001

whence $10^7\Sigma\Delta B/\Sigma w_2 = 11{\cdot}4$

1-Acetylanthracene in carbon tetrachloride

10^6w_2	2682	3521	4024	4382	4851	5093	5473	8329
$10^4\Delta\varepsilon$	207	264	300	330	356	378	408	625
$-10^5\Delta d$	147	187	219	237	260	268	298	441
$10^4\Delta n$	10	13	15	17	20	20	23	34
$10^{11}\Delta B$	278	360	401	465	494	545	571	897

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 7{\cdot}48$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}388$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}396$; $\Sigma\Delta n^2/\Sigma w_2 = 1{\cdot}155$; $10^7\Sigma\Delta B/\Sigma w_2 = 10{\cdot}5$

1,5-Diacetylnaphthalene in carbon tetrachloride

10^6w_2	2231	2925	3462	4191	5255
$10^4\Delta\varepsilon$	116	146	177	203	252
$-10^5\Delta d$	119	156	187	223	275
$10^4\Delta n$	6	8	10	11	14
$-10^{11}\Delta B$	366	478	574	697	881

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 4{\cdot}95$; $\Sigma\Delta d/E w_2 = -0{\cdot}531$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}271$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}791$; $10^7\Sigma\Delta B/\Sigma w_2 = -16{\cdot}6$

1,5-Diacetylanthracene in benzene

10^6w_2	2055	2388	2471	2604	3125	3444
$10^4\Delta\varepsilon$	56	62	63	76	78	96
10^6w_2	3554	4428	4707	4781	4800	
$10^4\Delta\varepsilon$	90	108	111	112	117	
10^6w_2	1464	2007	2102	2533	2623	2896
$10^5\Delta d$	41	53	56	65	66	78
$10^4\Delta n$	3	4	4	5	5	5

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}526$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}263$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}191$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}572$

1,5-Diacetylanthracene in carbon tetrachloride

10^6w_2	228	262	306
$-10^{11}\Delta B$	43	49	54

whence $10^7\Sigma\Delta B/\Sigma w_2 = -18{\cdot}3$

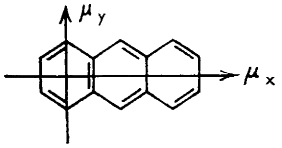
Results.—These are listed in usual form in Tables 1 and 2. The symbols are those previously explained.[5,6,8]

Previous Measurements.—The molar Kerr constant of 1-acetylnaphthalene is somewhat lower than that reported[9] previously (+341), presumably owing to the presence of a little of the 2-isomer in the earlier sample. No data are on record for the other compounds examined.

DISCUSSION

Calculation of Molar Kerr Constants.—Standard procedures[6b,c,10] are used to obtain theoretical molar Kerr constants by addition of bond and group polarisability tensors. Anisotropic polarisabilities * used in calculations are summarised in Table 3. We have assumed valence angles of 120° around the carbonyl carbon, and that the carbonyl group moment acts along the C=O link.

Principal Polarisabilities of the 1-*Anthryl Group.*—From measurements of the depolarisation ratio of scattered light, Lapouyade and Bothorel[11] determined the anisotropy in the polarisability tensors of several 1- and 9-substituted anthracenes. They reported that the anisotropies of the 1- and 9-substituted molecules were not equal, with the 9-substituted anthracene consistently being more anisotropic. Comparison of the molar Kerr constants of 1-chloro- and 1-cyano-anthracene (+229, +870) with those reported previously[12,13] for 9-chloro- and 9-cyano-anthracene (+172, +787) suggests that the anisotropy could be larger in the 1-substituted molecules. However, we have observed larger dipole moments in the 1-substituted anthracenes, and these may account for the larger Kerr constants. Because of the asymmetry of the 1-anthryl group, the directions of the two principal



(I)

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* Polarisabilities quoted throughout in 10^{-24} cm.^{3} (Å^3) and molar Kerr constants in 10^{-12} e.s.u.

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[12] R. J. W. Le Fèvre, L. Radom, and G. L. D. Ritchie, *J. Chem. Soc.*, 1968, 775.

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TABLE 2

Polarisations, refractions, dipole moments, and molar Kerr constants calculated from Table 1

Solute	Solvent	$\alpha\varepsilon_1$	β	$\gamma' n^2_1$	$_\infty P_2$ (cm.^{3})	R_D (cm.^{3})	μ (D) *	γ	δ	$10^{12}{}_\infty({}_mK_2)$
1-Chloroanthracene	CCl_4	3·05	−0·257	1·099	117·7	72·0	1·43	0·259	+144	+229
1-Cyanoanthracene	CCl_4	17·58	−0·362	1·360	429·3	78·4	4·14	0·322	+579	+870
1-Acetylnaphthalene	CCl_4	10·32 †	−0·399 †				2·89 †	0·185 †	+163	+203
1-Acetylanthracene	CCl_4	7·48	−0·338	1·155	228·6	79·0	2·67	0·272	+150	+243
1,5-Diacetylnaphthalene	CCl_4	4·95	−0·335	0·791	163·2	67·4	2·13	0·186	−237	−379
1,5-Diacetylanthracene ...	CCl_4								−260	−500
1,5-Diacetylanthracene ...	C_6H_6	2·53	0·301	0·572	187·1	90·1	2·13			

* Calculating assuming $_DP = 1·05\ R_D$. † Ref. 9.

axes lying in the aromatic plane may not coincide with those of the 9-anthryl group. There is thus the possibility that the moment along the C–X link (μ_Y) induces a moment (μ_X) in the highly polarisable long axis of anthracene [see (I)], so that the resultant moment is not directed along the 1,4-axis of the molecule. We have taken the value of the dipole moment of the 9-substituted molecule μ_Y, and by using the polarisabilities for anthracene derived from 9-substituted anthracenes, we have calculated the induced moments μ_X required to give agreement between the molar Kerr constants of the 1- and 9-substituted molecules. The resultant moments, μ(calc.), derived from μ_X and μ_Y are compared with the observed values, μ(obs.), in Table 4. The reasonable agreement between observed and calculated values suggests that the anthryl group polarisabilities derived from data on 9-substituted anthracenes are, to a fair approximation, applicable to 1-substituted anthracenes. We have therefore used these in the calculations which follow.

TABLE 3

Anisotropic polarisabilities of bonds, groups and molecules

	b_L	b_T	b_V	Ref.
C–H	0·65	0·65	0·65	*a*
C–C	0·97	0·26	0·26	*a*
C=O	2·30	1·40	0·46	*b*
1-Anthryl	23·81	35·25	15·23	12
1-Naphthyl	15·95	21·15	10·65	*c*
9-Chloroanthracene	27·84	37·32	16·88	12
9-Cyanoanthracene	30·41	36·52	17·42	13

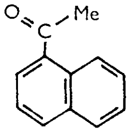
[a] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, *J. Chem. Soc.* (*B*), 1966, 273. [b] C. G. Le Fèvre, R. J. W. Le Fèvre, and B. P. Rao, *J. Chem. Soc.*, 1959, 2340. [c] R. J. W. Le Fèvre and L. Radom, *J. Chem. Soc.*, 1967, 1295.

TABLE 4

Dipole moment components in substituted anthracenes

	μ_Y	μ_X	μ(calc.)	μ(obs.)
1-Chloroanthracene ...	1·36	0·59	1·48	1·43
1-Cyanoanthracene ...	4·13	0·77	4·20	4·14

1-*Acetylnaphthalene*.—Molar Kerr constants have been calculated for various conformations of 1-acetylnaphthalene defined by the angle, θ, between the planes of the C–CO–C group and the aromatic nucleus. Conformations in which the C=O link is directed away from (II), and towards (III), the naphthalene nucleus but having the same value of θ, have identical theoretical Kerr constants. However, because of the smaller size of the oxygen compared with the methyl of the acetyl group, the latter situation (III) is considered the more likely.



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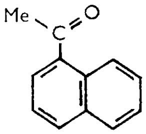


(III)

Comparison of the calculated Kerr constants (Table 5) with the observed (+203) suggests an effective conformational angle of 42° for 1-acetylnaphthalene.

TABLE 5

Molar Kerr constants of 1-acetylnaphthalene

θ:	0°	42°	45°	90°
$_m$K	+705	+210	+148	−410

1-*Acetylanthracene*.—Calculated molar Kerr constants for 1-acetylanthracene are shown in Table 6; the angle θ is as defined for 1-acetylnaphthalene. Comparison with the observed value (+243) indicates an effective conformational angle of 46° for this molecule. This result is close to the angle (42°) obtained for 1-acetylnaphthalene in which the steric situation is very similar.

TABLE 6

Molar Kerr constants for 1-acetylanthracene

θ:	0°	45°	46°	90°
$_mK$	+1179	+260	+236	−658

1,5-*Diacetylnaphthalene*.—Because of the results for 1-acetylnaphthalene and 1-acetylanthracene, we have assumed that in 1,5-diacetylnaphthalene the C–CO–C planes are inclined at approximately 45° to the aromatic plane. Further, we have considered only the isomers in which each acetyl group is in the sterically more favourable orientation (III). These two forms [represented schematically in the projection diagrams (IV) and (V)] may then be classified as *cis* (IV) and *trans* (V) and their dipole moments and molar Kerr constants are shown in Table 7. In addition, the mole fractions χ_{cis} and χ_{trans} derived from the dipole moment and Kerr constant data are included. The experimental results for 1,5-diacetylnaphthalene are thus consistent with a mixture of *cis* (38%) and *trans* (62%) conformers in which the planes of the C–CO–C groups are inclined at approximately 45° to the naphthalene plane.

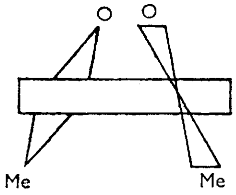
1,5-*Diacetylanthracene*.—Because of the low solubility of this compound in carbon tetrachloride the dipole

TABLE 7

Dipole moments and molar Kerr constants for conformations of 1,5-diacetylnaphthalene

	μ (D)	$_{\mathrm{m}}K$
cis	3·43	−1110
trans	0	+50
Observed	2·13	−379
χ_{cis}	0·39	0·37
χ_{trans}	0·61	0·63

moment was measured in benzene. However, the compound was sufficiently soluble in carbon tetrachloride for an estimate of the Kerr constant to be made in this solvent. The results have again been interpreted in terms of *cis* (IV) and *trans* (V) forms in which the angle between the C–CO–C planes and the aromatic plane is 45°.



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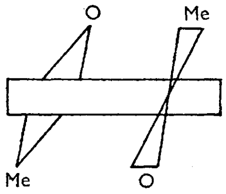

(V)

Calculated and observed quantities are summarised in Table 8.

TABLE 8

Dipole moments and molar Kerr constants for conformations of 1,5-diacetylanthracene

	μ (D)	$_{\mathrm{m}}K$
cis	3·43	−1834
trans	0	+157
Observed	2·13	−500
χ_{cis}	0·39	0·33
χ_{trans}	0·61	0·67

In this case, the experimental molar Kerr constant and dipole moment are consistent with the presence of *ca.* 36% of the *cis*-form. The result is close to that (38% *cis*) obtained for the analogous and sterically similar naphthalene derivative. For both 1,5-diacetylnaphthalene and 1,5-diacetylanthracene the *trans*-conformer is more favoured than the polar *cis*-form, as would be predicted.

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