932. *Molecular Polarisability: The Molar Kerr Constants and Dipole Moments of Sixteen Monosubstituted Naphthalenes.*

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It is shown that previous determinations of the anisotropy of polarisability of naphthalene, and of various bonds in combination with phenyl, can—provided exaltation effects are also included—lead to correct predictions of molar Kerr constants of naphthalene derivatives. The C–C–C and C–C–X angles in $C_{10}H_7X$ are assumed to be 120°. Non-planar conformations are indicated when X = α- or β-MeO, α-CHO, α-COMe, α-NO_2, and α- or β-NH_2; for the remaining cases, nearly flat structures appear satisfactory.

LE FÈVRE and LE FÈVRE [1] reported the molar Kerr constants, $_{\infty}({}_{m}K_2)$, dielectric polarisations, $_{\infty}P_2$, apparent dipole moments, μ, etc., of naphthalene and its eight monohalogeno-derivatives at infinite dilution in carbon tetrachloride. The present paper records

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[1] Le Fèvre and Le Fèvre, *J.*, 1955, 1641.

measurements on a further sixteen monosubstituted naphthalene derivatives, for several of which possibilities of rotational isomerism exist. Other evidence [2-4] suggests that the 8-hydrogen atom is more sterically affected by a bulky group in the 1-position than are the 1- or the 3-hydrogen atom by the same group in position 2, and that the " average " conformation of such a group, if unsymmetrical, may be determined thereby. Isomers related in the s-*cis*-s-*trans* sense [5] usually differ in the anisotropies of their polarisabilities, the assessment of which therefore provides a method of special value for the investigation of solute structures of this kind; [6,7] examples involving hydroxy-, methoxy-, dialkylamino-, etc., derivatives of benzene are given in refs. 8—10.

EXPERIMENTAL

Materials.—Commercial samples of the following were recrystallised or redistilled, as appropriate, immediately before use: 1- and 2-methylnaphthalene, methyl 1-naphthyl ether, methyl 1- and 2-naphthyl ketone, 1-naphthonitrile, 2-naphthaldehyde, 1-nitronaphthalene, and 1- and 2-naphthylamines. Methyl 2-naphthyl ether and 2-naphthonitrile were prepared as described by Vogel,[11] 1-naphthaldehyde by Badger's method,[12] and 2-nitronaphthalene by that of Hodgson and Marsden.[13] M. p.s or b. p.s of the specimens taken as solutes were as tabulated.

		Lit. (ref.)
1-$C_{10}H_7$·CH_3	b. p. 245°	244·6° (14)
2- ,, (from aq. EtOH)	m. p. 35°	36° (14)
1-$C_{10}H_7$·OH ,, ,,	m. p. 94°	94° (15)
2- ,, ,, ,,	m. p. 121°	122° (15)
1-$C_{10}H_7$·CO·CH_3	b. p. 180°/*ca.* 20 mm.	166—167°/12 mm. (11)
2- ,,	b. p. 190°/*ca.* 20 mm.	170—171°/11 mm. (11)
1-$C_{10}H_7$·CN	b. p. 170°/*ca.* 20 mm.	166—169°/18 mm. (11)
2- ,, (from ligroin)	m. p. 66°	66° (16)
1-$C_{10}H_7$·OCH_3	b. p. 260°	258° (17)
2- ,, (from C_6H_6)	m. p. 71°	72° (18)
1-$C_{10}H_7$·CHO	b. p. 160°/*ca.* 20 mm.	150°/13 mm. (11)
2- ,, (from H_2O)	m. p. 61°	59° (16)
1-$C_{10}H_7$·NO_2 (from EtOH)	m. p. 56°	55·8° (16)
2-$C_{10}H_7$·NO_2 (from aq. EtOH)	m. p. 80°	79° (16)
1-$C_{10}H_7$·NH_2	m. p. 50°	50° (15)
2- ,,	m. p. 112°	112° (15)

Apparatus, Procedures, Observations, etc.—Details of the measurement and interpretation of molar Kerr constants are given in refs. 7(*a*—*d*) and of dipole moments in ref. 19. Symbols and methods of calculation used here are explained in refs. 7 and 19, and summarised in ref. 20.

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[2] Everard and Sutton, *J.*, 1949, 2312.

[3] Batsanov and Pakhomov, *Vestnik Moskov. Univ.*, 1956, **11**, No. 2, *Ser. Fiz.-Mat. i Estestven. Nauk*, No. 1, 65.

[4] Merkel and Wiegand, *Naturwiss.*, 1947, **34**, 122.

[5] Mulliken, *Rev. Mod. Physics*, 1942, **14**, 265.

[6] Le Fèvre, *J. Proc. Roy. Soc. N.S.W.*, 1961, **95**, 1.

[7] Le Fèvre and Le Fèvre, (*a*) *Rev. Pure Appl. Chem.*, 1955, **5**, 261; (*b*) *J.*, 1953, 4041; (*c*) *J.*, 1954, 1577; (*d*) Chap. XXXVI in " Physical Methods of Organic Chemistry," ed. Weissberger, Interscience Publ. Inc., New York, London, 3rd edn., Vol. I, p. 2459.

[8] Le Fèvre and Williams, *J.*, 1960, 1825.

[9] Aroney and Le Fèvre, *J.*, (*a*) 1956, 2775; 1960, 2161, 3600; (*b*) 1958, 3002.

[10] Aroney, Le Fèvre, and Shu-Sing Chang, *J.*, 1960, 3173.

[11] Vogel, " Practical Organic Chemistry," Longmans, Green and Co., London, 3rd edn., 1956.

[12] Badger, *J.*, 1941, 535.

[13] Hodgson and Marsden, *J.*, 1947, 127.

[14] " Physical and Thermodynamic Properties of Hydrocarbons," A.P.I. Res. Project 44, Carnegie Press, 1953.

[15] Landolt–Börnstein, " Tabellen," 1912.

[16] Beilstein's " Handbuch der Organischen Chemie."

[17] International Critical Tables, 1930.

[18] Heilbron and Bunbury, " Dictionary of Organic Compounds," Eyre and Spottiswood, London, 1953.

[19] Le Fèvre, " Dipole Moments," Methuen, London, 3rd edn., 1953.

[20] Le Fèvre and Sundaram, *J.* 1962, 4003.

Observations and results are in Tables 1—3. Table 1 shows data from which are deduced the molar Kerr constants, dipole moments, polarisations, etc., listed in Tables 2 and 3.

TABLE 1.

Values of Δn, Δn^2, Δd, $\Delta\varepsilon$, and ΔB for solutions in carbon tetrachloride (except where specified as benzene) at 25°.

Solute: 1-Methylnaphthalene

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
1403	—	—	1202	—	—
2812	68	200	2430	—	94
3398	—	—	2956	—	—
4518	109	321	3848	—	147
5792	—	—	4942	—	—
6750	163	481	5732	—	212
8818	215	611	—	701	295
9909	242	691	—	797	325
13,089	315	908	—	1041	533
15,770	370	1079	—	1246	—

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}240$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}696$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}8556$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 0{\cdot}795$; $\Sigma\Delta B/\Sigma w_2 = 3{\cdot}31 \times 10^{-7}$.

Solute: 2-Methylnaphthalene

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
2668	65	191	2357	266	139
4398	103	303	3869	449	210
5939	148	436	5173	601	290
7460	186	548	6445	748	361
8686	213	628	7485	884	420
9512	227	670	8174	962	466

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}244$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}718$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}8666$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 1{\cdot}01$; $\Sigma\Delta B/\Sigma w_2 = 4{\cdot}87_7 \times 10^{-7}$.

Solute: 1-Naphthol

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
342	—	—	—	108	—
565	17	50	300	—	55
681	—	—	—	219	—
819	24	71	435	—	84
827	—	—	—	263	—
1032	—	—	—	330	—
1163	35	103	620	—	128
1349	41	121	717	—	145
1657	53	156	930	—	182

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}306$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}902$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}5406$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 3{\cdot}19$; $\Sigma\Delta B/\Sigma w_2 = 10{\cdot}7 \times 10^{-7}$

Solute: 2-Naphthol

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
111	4	12	60	—	—
225	7	21	119	—	24
232	—	—	—	75	—
287	9	27	153	—	36
298	—	—	—	97	—
301	—	—	161	—	37
377	—	—	—	119	—
386	12	36	205	—	47
392	—	—	—	129	—

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}317$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}951$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}5328$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 3{\cdot}23$; $\Sigma\Delta B/\Sigma w_2 = 12{\cdot}03 \times 10^{-7}$.

Solute: 1-Methoxynaphthalene

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
1390	—	—	—	—	124
1523	35	103	—	—	—
1954	—	—	—	—	181
2418	55	161	1633	585	214
4021	90	264	2701	1068	355
4535	101	297	3028	1235	405
5970	133	391	4004	1632	—
7030	159	468	4687	1900	—

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}225$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}661$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}6696$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}67_8$; $\Sigma\Delta B/\Sigma w_2 = 8{\cdot}93 \times 10^{-7}$.

Solute: 2-Methoxynaphthalene

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
521	—	—	—	117	—
817	—	—	—	188	—
1221	—	—	—	279	—
1541	—	—	—	—	65
1749	35	102	1185	—	72
1842	—	—	—	414	—
2629	55	161	1802	—	109
3859	78	229	2627	—	160
4690	98	288	3204	—	195
5625	117	344	3848	—	235

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}206$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}606$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}4309$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}27$; $\Sigma\Delta B/\Sigma w_2 = 4{\cdot}17 \times 10^{-7}$.

Solute: 1-Naphthaldehyde

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
142	—	—	—	—	49
310	—	—	—	—	97
408	—	—	—	—	137
506	—	—	—	—	174
590	—	—	—	—	198
937	33	96	539	1040	—
1634	57	167	941	1830	—
2393	83	243	1359	2692	—
3342	117	342	1906	3790	—
4114	144	422	2361	4670	—

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}349$; $\Sigma\Delta n^2/\Sigma w_2 = 1{\cdot}023$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}5721$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 11{\cdot}29$; $\Sigma\Delta B/\Sigma w_2 = 33{\cdot}49 \times 10^{-7}$.

Solute: 2-Naphthaldehyde

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
102	—	—	—	—	76
193	—	—	—	—	147
242	—	—	—	—	177
296	—	—	—	—	220
339	—	—	—	—	250
827	26	76	481	1100	—
1557	51	149	921	2064	—
2486	81	237	1432	3326	—
3424	109	319	1988	4487	—
4215	138	404	2439	5543	—

whence $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}324$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}947$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}5805$; $\Sigma\Delta\varepsilon/\Sigma w_2 = 13{\cdot}2_1$; $\Sigma\Delta B/\Sigma w_2 = 74{\cdot}2_3 \times 10^{-7}$.

TABLE 1. (*Continued.*)

Solute: 1-Acetylnaphthalene.

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
343	—	—	—	—	66
507	—	—	—	—	102
636	—	—	—	—	123
872	24	70	555	851	163
1021	—	—	—	—	192
1340	—	—	—	—	251
1447	40	117	917	1488	—
2329	65	191	1507	2401	—
3156	84	247	1996	3290	—
4236	112	329	2642	4393	—

whence $\sum\Delta n/\sum w_2 = 0{\cdot}270$; $\sum\Delta n^2/\sum w_2 = 0{\cdot}792$; $\sum\Delta d/\sum w_2 = -0{\cdot}6326$; $\sum\Delta\varepsilon/\sum w_2 = 10{\cdot}32$; $\sum\Delta B/\sum w_2 = 19{\cdot}00 \times 10^{-7}$.

Solute: 2-Acetylnaphthalene.

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
111	—	—	—	—	59
168	—	—	—	—	86
260	—	—	—	—	130
339	—	—	—	—	180
435	—	—	270	—	229
520	—	—	—	—	280
629	—	—	393	—	—
738	—	—	460	—	—
911	22	65	568	1122	—
1462	34	100	928	1790	—
1947	48	141	1243	2362	—
2144	51	150	—	2626	—
2549	61	180	—	3126	—

whence $\sum\Delta n/\sum w_2 = 0{\cdot}240$; $\sum\Delta n^2/\sum w_2 = 0{\cdot}706$; $\sum\Delta d/\sum w_2 = -0{\cdot}6308$; $\sum\Delta\varepsilon/\sum w_2 = 12{\cdot}2_3$; $\sum\Delta B/\sum w_2 = 52{\cdot}6_4 \times 10^{-7}$.

Solute: 1-Naphthonitrile

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
153	3	9	97	318	89
264	5	15	165	545	170
330	7	21	228	683	228
516	12	35	345	1071	342
628	15	44	389	1309	425
730	18	53	469	1515	485

whence $\sum\Delta n/\sum w_2 = 0{\cdot}229$; $\sum\Delta n^2/\sum w_2 = 0{\cdot}675$; $\sum\Delta d/\sum w_2 = -0{\cdot}6459$; $\sum\Delta\varepsilon/\sum w_2 = 20{\cdot}76$; $10^7\Delta B = 64{\cdot}9_5w_2 + 290w_2^2$.

Solute: 2-Naphthonitrile.

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
122	—	—	—	299	205
183	—	—	—	444	330
234	—	—	—	570	430
274	—	—	—	666	511
309	—	—	—	754	557
352	—	—	—	858	640
645	16	47	392	—	—
1075	29	85	652	—	—
1832	48	141	1173	—	—
2241	58	170	1400	—	—
2730	71	208	1717	—	—
3142	83	244	2009	—	—

whence $\sum\Delta n/\sum w_2 = 0{\cdot}262$; $\sum\Delta n^2/\sum w_2 = 0{\cdot}767$; $\sum\Delta d/\sum w_2 = -0{\cdot}6295$; $\sum\Delta\varepsilon/\sum w_2 = 24{\cdot}36$; $\sum\Delta B/\sum w_2 = 181{\cdot}4 \times 10^{-7}$.

Solute: 1-Nitronaphthalene.

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
111	—	—	54	204	52
185	—	—	89	342	93
267	—	—	127	496	141
359	—	—	170	656	203
438	—	—	208	810	231
553	14	41	—	—	293
923	24	71	—	—	
1366	36	106	—	—	—
1734	44	130	—	—	—
2210	56	165	—	—	—
2695	68	201	—	—	—

whence $\sum\Delta n/\sum w_2 = 0{\cdot}255$; $\sum\Delta n^2/\sum w_2 = 0{\cdot}753$; $\sum\Delta d/\sum w_2 = -0{\cdot}4765$; $\sum\Delta\varepsilon/\sum w_2 = 18{\cdot}44$; $\sum\Delta B/\sum w_2 = 52{\cdot}90 \times 10^{-7}$.

Solute: 2-Nitronaphthalene.

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
89	—	—	41	200	132
128	—	—	60	285	185
189	—	—	88	421	272
226	—	—	105	505	337
257	—	—	119	574	379
327	—	—	153	729	470
672	18	53	—	—	—
1064	28	82	—	—	—
1321	34	100	—	—	—
1639	43	126	—	—	—
1811	48	141	—	—	—
2024	56	165	—	—	—

whence $\sum\Delta n/\sum w_2 = 0{\cdot}266$; $\sum\Delta n^2/\sum w_2 = 0{\cdot}782$; $\sum\Delta d/\sum w_2 = -0{\cdot}4655$; $\sum\Delta\varepsilon/\sum w_2 = 22{\cdot}32$; $\sum\Delta B/\sum w_2 = 146{\cdot}1 \times 10^{-7}$.

Solute: 1-Naphthylamine. Solvent: Benzene.

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
828	—	—	—	—	27
1137	17	51	−228	252	—
1407	—	—	—	—	45
1623	—	—	—	—	52
1836	—	—	—	—	60
2085	32	96	−436	461	—
2748	42	126	−576	607	—
3284	51	153	−683	729	—
4315	66	198	−902	962	—
6020	91	273	−1270	1338	—

whence $\sum\Delta n/\sum w_2 = 0{\cdot}153$; $\sum\Delta n^2/\sum w_2 = 0{\cdot}458$; $\sum\Delta d/\sum w_2 = +0{\cdot}2090$; $\sum\Delta\varepsilon/\sum w_2 = 2{\cdot}22$; $\sum\Delta B/\sum w_2 = 3{\cdot}23 \times 10^{-7}$.

Solute: 2-Naphthylamine. Solvent: Benzene.

10^5w_2	$10^4\Delta n$	$10^4\Delta n^2$	$-10^5\Delta d$	$10^4\Delta\varepsilon$	$10^{10}\Delta B$
636	—	—	—	—	18
829	12	36	−174	242	—
963	—	—	—	—	27
1385	20	60	−294	406	—
1407	—	—	—	—	40
1638	—	—	—	—	46
2438	36	108	−519	714	—
3693	54	162	−782	1075	—
4211	62	186	−897	1229	—

whence $\sum\Delta n/\sum w_2 = 0{\cdot}147$; $\sum\Delta n^2/\sum w_2 = 0{\cdot}440$; $\sum\Delta d/\sum w_2 = 0{\cdot}2123$; $\sum\Delta\varepsilon/\sum w_2 = 2{\cdot}9_2$; $\sum\Delta B/\sum w_2 = 2{\cdot}82 \times 10^{-7}$.

TABLE 2.

Total polarisations at infinite dilution, molecular refractions and dipole moments calculated from Table 1.

Solute	$\alpha\varepsilon_1$	β	$\gamma' n_1^2$	M_2	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) *
1-$C_{10}H_7{\cdot}CH_3$	$0{\cdot}79_5$	$-0{\cdot}5400$	0·696	142·2	52·1	$48{\cdot}6_5$	$0{\cdot}22_3$
2- ,,	1·01	$-0{\cdot}5469$	0·718	142·2	55·5	$49{\cdot}1_4$	0·44
1-$C_{10}H_7{\cdot}OH$	3·19	$-0{\cdot}3412$	0·902	144·2	84·2	47·7	1·29
2- ,,	3·23	$-0{\cdot}3363$	0·951	144·2	84·7	$48{\cdot}3_6$	1·29
1-$C_{10}H_7{\cdot}OCH_3$	2·68	$-0{\cdot}4226$	0·661	158·1	$86{\cdot}0_5$	50·3	$1{\cdot}27_4$
2- ,,	2·27	$-0{\cdot}4309$	0·606	158·1	79·5	49·6	1·16
1-$C_{10}H_7{\cdot}CHO$	11·29	$-0{\cdot}3611$	1·023	156·2	225·8	$54{\cdot}3_6$	2·87
2- ,,	13·21	$-0{\cdot}3664$	0·947	156·2	$257{\cdot}7_4$	53·2	3·14
1-$C_{10}H_7{\cdot}CO{\cdot}CH_3$	10·32	$-0{\cdot}3992$	0·792	170·2	229·5	55·9	2·89
2- ,,	12·23	$-0{\cdot}3981$	0·706	170·2	263·8	$54{\cdot}2_4$	3·18
1-$C_{10}H_7{\cdot}CN$	20·76	$-0{\cdot}4076$	0·675	153·2	376·5	48·6	3·99
2- ,,	24·36	$-0{\cdot}3973$	0·767	153·2	434·7	49·9	4·32
1-$C_{10}H_7{\cdot}NO_2$	18·44	$-0{\cdot}3007$	0·753	173·2	379·7	53·3	3·98
2- ,,	22·32	$-0{\cdot}2938$	0·782	173·2	450·7	53·6	4·39
1-$C_{10}H_7{\cdot}NH_2$ †	2·22	$+0{\cdot}2392$	0·458	143·2	96·9	49·0	1·49
2- ,, †	2·92	$+0{\cdot}2430$	0·440	143·2	115·6	$48{\cdot}3_4$	1·78

* μ is determined in all cases taking $_DP$ as $1{\cdot}05R_D$. † 1- and 2-Naphthylamine were measured in benzene.

TABLE 3.

Molar Kerr constants at infinite dilution calculated from Tables 1 and 2 together with calculated molar refractions and exaltations.

Solute	γ	δ	$_\infty(_mK_2)\ .\ 10^{12}$	R_D (calc.) *	R_D (calc.) †	$10^{23}\Delta b$ ‡
1-$C_{10}H_7{\cdot}CH_3$	0·165	47·30	51·43	49·0	47·6	$-0{\cdot}042$
2- ,,	0·167	69·67	75·05	,,	,,	$+0{\cdot}017$
1-$C_{10}H_7{\cdot}OH$	0·210	152·9	164·7	45·9	44·5	$+0{\cdot}214$
2- ,,	0·218	171·9	185·2	,,	,,	$+0{\cdot}293$
1-$C_{10}H_7{\cdot}OCH_3$	0·154	127·6	151·1	50·8	49·4	$-0{\cdot}059$
2- ,,	0·142	59·51	70·72	,,	,,	$-0{\cdot}143$
1-$C_{10}H_7{\cdot}CHO$	0·239	478·4	554·5	49·0	47·6	$+0{\cdot}637$
2- ,,	0·216	1060	1235	,,	,,	$+0{\cdot}499$
1-$C_{10}H_7{\cdot}CO{\cdot}CH_3$	0·185	271·5	341·0	53·8	52·4	$+0{\cdot}250$
2- ,,	0·164	752·0	951·7	,,	,,	$+0{\cdot}052$
1-$C_{10}H_7{\cdot}CN$	0·157	928·0	1054	48·8	47·4	$-0{\cdot}024$
2- ,,	0·179	2591	2961	,,	,,	$+0{\cdot}131$
1-$C_{10}H_7{\cdot}NO_2$	0·175	755·7	970·4	50·9	49·5	$+0{\cdot}285$
2- ,,	0·183	2086	2694	,,	,,	$+0{\cdot}321$
1-$C_{10}H_7{\cdot}NH_2$ §	0·102	7·88	81·1	47·8	46·4	$+0{\cdot}143$
2- ,,	0·098	6·88	66·7	,,	,,	$+0{\cdot}064$

* Calc. by using R_D of naphthalene and Vogel's data. † Calc. by using C_{Ar}–C_{Ar} from Vogel's data. ‡ Calc. as $[R_D\ (\text{obs.}) - R_D(\text{calc.})] \times 0{\cdot}11891 = 10^{-23}\Delta b$. § Determined in benzene.

TABLE 4.

Dipole moments published since 1948.

Solute	Solvent	μ (D)	Authors
1-$C_{10}H_7{\cdot}CH_3$	(Liquid)	0·51	Rampolla and Smyth [21]
,,	C_6H_6	0·28	Luther and Operskalski [22]
,,	C_6H_6	0·23	Sahney *et al.*[23]
2-$C_{10}H_7{\cdot}CH_3$	(Liquid)	0·42	Rampolla and Smyth [21]
,,	C_6H_6	0·44	Luther and Operskalski [22]
1-$C_{10}H_7{\cdot}OH$	C_6H_6	1·39	Sahney *et al.*[23]
2-$C_{10}H_7{\cdot}OH$	C_6H_6	1·41	,,
1-$C_{10}H_7{\cdot}OCH_3$	C_6H_6	1·28 ± 0·03	Everard and Sutton [2]
1-$C_{10}H_7{\cdot}NO_2$	C_6H_6	4·00	Rampolla and Smyth [21]
,,	,,	3·98	Chau and Le Fèvre [24]
,,	$C_6H_5{\cdot}CH_3$	3·87	,, ,,
,,	CCl_4	4·00	,, ,,
,,	Dioxan	3·90	,, ,,
,,	C_6H_6	3·68	Sahney *et al.*[23]
1-$C_{10}H_7{\cdot}NH_2$	C_6H_6	1·78	,,
2-$C_{10}H_7{\cdot}NH_2$	C_6H_6	$1{\cdot}90_4$	,,

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[21] Rampolla and Smyth, *J. Amer. Chem. Soc.*, 1958, **80**, 1057.

[22] Luther and Operskalski, *Naturwiss.*, 1950, **37**, 376.

[23] Sahney, Beri, Sarma, and Singh, *J. Indian Chem. Soc.*, 1949, **26**, 329.

[24] Chau and Le Fèvre, *J.*, 1957, 2300.

DISCUSSION

Dipole Moments.—Dipole moments for nine of the sixteen substances listed in Table 2 have been reported previously. The literature since 1948 contains the values in Table 4. Measurements made before 1948 are given by Wesson;[25] they concern only nitronaphthalenes, naphthols, and naphthylamines, and differ considerably among themselves (Table 5). Our results fall almost within the limits of Table 5, and disagree significantly with the moments of Table 4 only for the naphthols and naphthylamines.

Molecular Refractions.—The R_D's of Table 3 have been calculated in two ways: either (*a*) the R_D of naphthalene, less the bond refraction appropriate[26] for C–H, or (*b*) Vogel's refractivities[26] alone ($11R_{C_{Ar}-C_{Ar}}$ plus $7R_{C-H}$), are taken as R_{naphthyl}, which is then added to $R_{C-\text{subst.}}$. Comparisons of the R_D's calculated and observed reveal differences exceeding experimental errors (which we estimate as ±0·3 c.c. on the average). Since the refractions computed by method (*a*) are closer to the measured values than are those by (*b*), the former have been used in estimating exaltations of polarisability Δb in these molecules. such Δb's are mostly larger than the corresponding quantities noted previously[7c] for monosubstituted benzenes; no generalisation regarding the relative magnitudes of Δb for α- and β-naphthalene derivatives can be drawn from Tables 2 and 3.

TABLE 5.

Dipole moments published before 1948.

Solute	μ (D)	Solute	μ (D)
$1\text{-}C_{10}H_7\cdot NO_2$	3·62—3·88	$2\text{-}C_{10}H_7\cdot OH$	1·3—1·53
$2\text{-}C_{10}H_7\cdot NO_2$	4·36—4·40	$1\text{-}C_{10}H_7\cdot NH_2$	1·44—1·53
$1\text{-}C_{10}H_7\cdot OH$	1·0—1·91	$2\text{-}C_{10}H_7\cdot NH_2$	1·73—2·10

Molar Kerr Constants.—The electric double refraction of none of the solutes in Tables 1 and 3 has been examined before. In all cases the $_\infty({}_mK_2)$ is positive; the 2-isomers have higher values than the 1-isomers except for the methoxy- and amino-naphthalenes. Data for 1- and 2-halogeno-naphthalenes have already been reported by Le Fèvre and Le Fèvre.[1]

We now proceed to attempt the calculation *a priori* of the molar Kerr constants to be expected for likely structures or conformations of these naphthalene derivatives. The anisotropic polarisabilities of the bonds involved are as listed in ref. 6, Table 1, and ref. 27, Table 5, the last-cited being longitudinal, transverse, and "vertical" polarisabilities (b_L^{XY}, b_T^{XY}, and b_V^{XY}, respectively) for bonds X–Y in combination with phenyl. The principal polarisabilities of the naphthyl group ($b_1^{C_{10}H_7}$, $b_2^{C_{10}H_7}$, and $b_3^{C_{10}H_7}$) are derived from the semi-axes of the polarisability ellipsoid deduced for naphthalene[1] together with those of the C–H link.[6] Computational methods are outlined in ref. 7*d* and described in detail in ref. 28. The exaltations Δb are assumed to operate in those directions where electromeric shifts should be easiest. For simplicity, all C–C–C angles of the naphthalene skeleton are regarded as 120°, and substituent C–X bonds are supposed to be likewise inclined towards their adjoining C_{Ar}–C_{Ar} bonds. Numerically the deviations from 120° shown for entry M 244 of ref. 29 do not significantly affect the calculations of ${}_mK$'s which now follow in the compound order adopted in Tables 1—3.

With 1- and 2-methylnaphthalene, when the polarisability ellipsoid reported by Le Fèvre and Rao[27] for the C–CH$_3$ unit is used, molecular semi-axes * emerge as in Table 6;

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* Molecular and bond polarisabilities are quoted throughout in 10^{-23} c.c. units; dipole moments or moment components are in D units.

[25] Wesson, "Tables of Electric Dipole Moments," Technology Press, Massachusetts Inst. Technology, 1948.

[26] Vogel, Cresswell, Jeffrey, and Leicester, *J.*, 1952, 514.

[27] Le Fèvre and Rao, *J.*, 1958, 1465.

[28] Eckert and Le Fèvre, *J.*, 1962, 1081.

[29] Sutton *et al.*, "Tables of Interatomic Distances and Configuration in Molecules and Ions," *Chem. Soc. Special Publ.*, No. 11, 1958.

TABLE 6.

Principal polarisabilities and moment components in 1- and 2-methylnaphthalene.

Molecule		Direction cosines with * OX	OY	OZ	
1-$C_{10}H_7{\cdot}CH_3$	$b_1 = 2{\cdot}436$	1	0	0	$\mu_1 = 0$
	$b_2 = 1{\cdot}921$	0	1	0	$\mu_2 = 0{\cdot}22_3$
	$b_3 = 1{\cdot}176$	0	0	1	$\mu_3 = 0$
2-$C_{10}H_7{\cdot}CH_3$	$b_1 = 2{\cdot}361$	+0·9976	+0·0698	0	$\mu_1 = 0{\cdot}395$
	$b_2 = 1{\cdot}931$	−0·0698	+0·9976	0	$\mu_2 = 0{\cdot}193$
	$b_3 = 1{\cdot}185$	0	0	1	$\mu_3 = 0$

* References axes *OX* and *OY* are in the molecular plane, *OY* is parallel to the 2,3-bond, and *OZ* is perpendicular to *OX* and *OY*.

addition of the exaltation equally to b_1 and b_2 then gives ${}_{\mathrm{m}}K$'s calc. of 58·7 and 72·5 × 10^{-12}, respectively. The observed values are 51·4 and 75·0$_5$ × 10^{-12}, so that our predictions are in error by *ca.* 14% and 3·4%. The discrepancy with 2-methylnaphthalene is tolerable, in view of the facts that the structural assumptions made may be oversimple and that hyperconjugation might occur to an unknown extent (compare the moments of the 1- and 2-methyl isomers, 0·22$_3$ and 0·44 D, and the remarks of Hoi and Daudel [30] on the former). As to 1-methylnaphthalene, we note that a Leybold model shows an overlap of the van der Waals zones of the methyl group and of the 8-hydrogen atom; in reality therefore the C–CH_3 bond may be deflected somewhat either towards the *OX*- or the *OZ*-axis, and both of these distortions will tend to reduce ${}_{\mathrm{m}}K$ calc.

With the 1- and 2-naphthols difficulties are encountered similar to those discussed [8] for phenols by Le Fèvre and Williams: neither the conformation of the COH unit nor the direction of action of $\mu_{\text{resultant}}$ is known with certainty. However, the following approach roughly meets the data from experiment. From the polarisability semi-axes of methanol, Le Fèvre *et al.*[31] deduced the three *b*'s for the COH fragment as 0·123, 0·171, and 0·086. These are relatively small compared with the corresponding quantities for the naphthyl radical; therefore, as an approximation, let the principal directions in COH be taken so that $b_{\mathrm{L}}^{\mathrm{COH}}$ is parallel to the C–O link in both naphthols and $b_{\mathrm{T}}^{\mathrm{COH}}$ is in the plane of the naphthyl group. Estimates for 1- and 2-naphthol then become:

	Direction cosines with * OX	OY	OZ		Direction cosines with * OX	OY	OZ
	1-Naphthol				2-Naphthol		
$b_1 = 2{\cdot}257$	1	0	0	$b_1 = 2{\cdot}219$	0·9973	0·0732	0
$b_2 = 1{\cdot}819$	0	1	0	$b_2 = 1{\cdot}857$	−0·0732	0·9973	0
$b_3 = 1{\cdot}052$	0	0	1	$b_3 = 1{\cdot}052$	0	0	1

* *OX*, *OY*, and *OZ* are as defined under Table 6.

To these are added the observed exaltations (Table 3), wholly to b_2 for 1-naphthol, and divided between b_1 and b_2 as cos² 30° : sin² 30° for 2-naphthol. Were $\mu_{\text{resultant}}$ acting along the C–O bond directions in the two cases the calculated molar Kerr constants (131 and 219 × 10^{-12}) would disagree with the measured quantities (164·6 and 183·5 × 10^{-12}); prediction and experiment can be reconciled if in the 1-isomer $\mu_{\text{resultant}}$ is inclined 47·5° (or 132·5°) to the C–O bond and in the 2-isomer if the corresponding angle is 68·8° (or 111·2°); $\mu_{\text{resultant}}$ in each structure being in the naphthalene plane. Then, respectively, we have:

1-Naphthol			2-Naphtho		
$b_1 = 2{\cdot}257$	$\mu_1 = 0{\cdot}95$	$10^{35}\theta_1 = 14{\cdot}65$	$b_1 = 2{\cdot}439$	$\mu_1 = 0{\cdot}944$	$10^{35}\theta_1 = 17{\cdot}55$
$b_2 = 2{\cdot}033$	$\mu_2 = 0{\cdot}87_3$	$10^{35}\theta_2 = 24{\cdot}51$	$b_2 = 1{\cdot}930$	$\mu_2 = 0{\cdot}880$	$10^{35}\theta_2 = 25{\cdot}93$
$b_3 = 1{\cdot}052$	$\mu_3 = 0$	${}_{\mathrm{m}}K$ calc. = 164·7 × 10^{-12}	$b_3 = 1{\cdot}052$	$\mu_3 = 0$	$10^{12}{}_{\mathrm{m}}K$ calc. = 182·8

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[30] Hoi and Daudel, *Rec. Trav. chim.*, 1946, **65**, 731.

[31] Le Fèvre, Le Fèvre, Rao, and Williams, *J.*, 1960, 123.

For comparison it may be noted that the angles 47·5° and 68·8° are analogous to those around 60° found satisfactory with alcohols [31] and somewhat less so with phenols.[8]

If the angles between C–O and $\mu_{\text{resultant}}$ are retained but the COH triangles are rotated into planes perpendicular to those of the naphthyl radicals, then the ${}_{\text{m}}K$'s calculated become algebraically negative (-50 and -92×10^{-12}) for both compounds; because of this we have preferred to regard the naphthols as nearly flat molecules. Inspection of Leybold models suggests no notable interference between hydroxyl groups in the 1- or 2-position and the hydrogen atoms of the $C_{10}H_7$ nucleus.

The steric situation is different for the methoxynaphthalenes. Everard and Sutton [2] concluded, from dipole moment studies, that the methoxy-group tends to lie in the plane of an aromatic ring to which it is attached, π-bonding from oxygen to the Ar-system being the cause conducive to flatness which, however, may not be completely achieved owing to overcrowding. With 1-methoxynaphthalene two planar conformations, A and B, can be imagined: in A the OMe unit is *cis* to the 8-H atom, and in B it is *trans*. Since resultant moments, polarisability ellipsoids, and molar Kerr constants should be identical for models A and B, present techniques are of use only in choosing between non-planar variants of these forms. Nevertheless, the stable existence of form A is less likely than of B, because in A the van der Waals zones of methyl and of the 8-hydrogen atom interpenetrate by *ca.* 1·1 Å, while in form B methyl and the 2-hydrogen atom do so by as little as 0·1 Å. The resultant dipole moment is taken as acting at 76° to the Aryl–O direction, *i.e.*, as suggested for anisole by Lumbroso.[32] Calculations are summarised in Table 7 for the planar forms (IA or B), and two non-planar versions of B, *viz.*, C in which the $C_{Ar}OMe$ triangle is in a plane at 90° to the naphthalene plane, and D in which this angle is 19° instead of 90°. The observed ${}_{\text{m}}K$ is 151×10^{-12}. A conformation such as D thus satisfactorily represents 1-methoxynaphthalene as a solute; it closely resembles that previously [10] given for anisole, in which a non-planarity of 18° was recognised.

TABLE 7.

Principal polarisabilities, moment components, etc., calculated for 1-methoxynaphthalene.

Model		Direction cosines with *			
		OX	*OY*	*OZ*	
A or B (planar)	$b_1 = 2{\cdot}393_5$	0·9995	0·0314	0	$\mu_1 = -1{\cdot}245$
	$b_2 = 2{\cdot}012_5$	−0·0314	0·9995	0	$\mu_2 = -0{\cdot}270$
	$b_3 = 1{\cdot}236$	0	0	1	$\mu_3 = 0$
whence $10^{35}\theta_1 = 12{\cdot}40_7$, $10^{35}\theta_2 = 31{\cdot}69$, and $10^{12}{}_{\text{m}}K$ calc. = 185·4; if Δb added to b_2, $10^{35}\theta_1 = 12{\cdot}17$, $10^{35}\theta_2 = 32{\cdot}78$, and $10^{12}{}_{\text{m}}K_{\text{calc.}} = 189$.					
C (non-planar)	$b_1 = 2{\cdot}356$	1	0	0	$\mu_1 = 0$
	$b_2 = 2{\cdot}013_3$	0	0·9998	0·0175	$\mu_2 = 0{\cdot}330$
	$b_3 = 1{\cdot}272$	0	−0·0175	0·9998	$\mu_3 = 1{\cdot}231$
whence $10^{35}\theta_1 = 10{\cdot}93$, $10^{35}\theta_2 = -35{\cdot}71$, and $10^{12}{}_{\text{m}}K_{\text{calc}} = -104{\cdot}2$; if Δb added to b_2, $10^{35}\theta_1 = 10{\cdot}69$, $10^{35}\theta_2 = -34{\cdot}71$, and $10^{12}{}_{\text{m}}K$ calc. = −101·0.					
D (non-planar)	$b_1 = 2{\cdot}388$	0·9994	0·0320	0·0112	$\mu_1 = -1{\cdot}16_4$
	$b_2 = 2{\cdot}015$	−0·0321	0·9995	0·0054	$\mu_2 = -0{\cdot}32_7$
	$b_3 = 1{\cdot}239$	−0·0110	−0·0058	0·9999	$\mu_3 = -0{\cdot}40_4$
whence $10^{35}\theta_1 = 12{\cdot}25$, $10^{35}\theta_2 = 23{\cdot}52$, and $10^{12}{}_{\text{m}}K$ calc. = 150; if Δb added to b_2, $10^{35}\theta_1 = 12{\cdot}01$, $10^{35}\theta_2 = 24{\cdot}54$, and $10^{12}{}_{\text{m}}K$ calc. = 154.					

* See formulæ (IA and B) for locations of *OX*, *OY*, and *OZ*.

The two flat extreme forms of 2-methoxynaphthalene (IIA and B) appear in scale drawings and models to be equally possible from the viewpoint of overlap between methyl and the 1- or the 3-hydrogen atom. The calculations reported in Table 8 refer, in addition to forms A and B, to the following: C, intermediate between A and B; D, in which the

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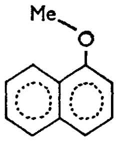
[32] Lumbroso, *Bull. Soc. chim. France*, 1950, **17**, 812; Lumbroso and Dumas, *ibid.*, 1955, 655.

TABLE 8.

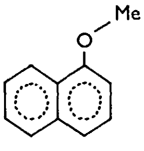
Principal polarisabilities, moment components, etc., calculated for 2-methoxynaphthalene.

<table>
<tr><th></th><th colspan="3">Direction cosines with</th><th></th><th></th></tr>
<tr><th>Model</th><th>OX</th><th>OY</th><th>OZ</th><th></th><th></th></tr>
<tr><td>A</td><td>$b_1 = 2{\cdot}389_3$</td><td>0·9996</td><td>0·0279</td><td>0</td><td>$\mu_1 = 0{\cdot}288$</td></tr>
<tr><td></td><td>$b_2 = 2{\cdot}016_7$</td><td>−0·0279</td><td>0·9996</td><td>0</td><td>$\mu_2 = -1{\cdot}124$</td></tr>
<tr><td></td><td>$b_3 = 1{\cdot}236$</td><td>0</td><td>0</td><td>1</td><td>$\mu_3 = 0$</td></tr>
<tr><td colspan="6">whence $10^{35}\theta_1 = 12{\cdot}35$, $10^{35}\theta_2 = 8{\cdot}43$, and $10^{12}{}_{\rm m}K$ calc. = 87·4; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 10{\cdot}34$, $10^{35}\theta_2 = 8{\cdot}82$, and $10^{12}{}_{\rm m}K$ calc. = 80·6.</td></tr>
<tr><td>B (planar)</td><td>$b_1 = 2{\cdot}412$</td><td>1</td><td>0</td><td>0</td><td>$\mu_1 = -0{\cdot}806$</td></tr>
<tr><td></td><td>$b_2 = 1{\cdot}994$</td><td>0</td><td>1</td><td>0</td><td>$\mu_2 = 0{\cdot}834$</td></tr>
<tr><td></td><td>$b_3 = 1{\cdot}236$</td><td>0</td><td>0</td><td>1</td><td>$\mu_3 = 0$</td></tr>
<tr><td colspan="6">whence $10^{35}\theta_1 = 12{\cdot}67$, $10^{35}\theta_2 = 16{\cdot}73$, and $10^{12}{}_{\rm m}K$ calc. = 124; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 10{\cdot}59$, $10^{35}\theta_2 = 15{\cdot}51$, and $10^{12}{}_{\rm m}K$ calc. = 110.</td></tr>
<tr><td>C (non-planar)</td><td>$b_1 = 2{\cdot}392_4$</td><td>0·9987</td><td>0·0491</td><td>0·0107</td><td>$\mu_1 = -0{\cdot}261$</td></tr>
<tr><td></td><td>$b_2 = 1{\cdot}976_8$</td><td>−0·0492</td><td>0·9988</td><td>0·0088</td><td>$\mu_2 = -0{\cdot}138$</td></tr>
<tr><td></td><td>$b_3 = 1{\cdot}272_8$</td><td>−0·0103</td><td>−0·0094</td><td>0·9999</td><td>$\mu_3 = -1{\cdot}122$</td></tr>
<tr><td colspan="6">whence $10^{35}\theta_1 = 11{\cdot}42$, $10^{35}\theta_2 = -28{\cdot}70$, and $10^{12}{}_{\rm m}K$ calc. = −72·7; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 9{\cdot}42$, $10^{35}\theta_2 = -26{\cdot}49$, and $10^{12}{}_{\rm m}K$ calc. = −71·8.</td></tr>
<tr><td>D (non-planar)</td><td>$b_1 = 2{\cdot}389$</td><td>0·9995</td><td>0·0313</td><td>−0·0016</td><td>$\mu_1 = 0{\cdot}274$</td></tr>
<tr><td></td><td>$b_2 = 2{\cdot}013$</td><td>−0·0313</td><td>0·9994</td><td>0·0165</td><td>$\mu_2 = -1{\cdot}086$</td></tr>
<tr><td></td><td>$b_3 = 1{\cdot}240$</td><td>0·0021</td><td>−0·0165</td><td>0·9999</td><td>$\mu_3 = -0{\cdot}321$</td></tr>
<tr><td colspan="6">whence $10^{35}\theta_1 = 12{\cdot}24$, $10^{35}\theta_2 = 5{\cdot}07$, and $10^{12}{}_{\rm m}K$ calc. = 72·8; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 10{\cdot}23$, $10^{35}\theta_2 = 5{\cdot}62$, and $10^{12}{}_{\rm m}K$ calc. = $66{\cdot}6_5$.</td></tr>
<tr><td>E (non-planar)</td><td>$b_1 = 2{\cdot}410$</td><td>0·9991</td><td>−0·0408</td><td>0·0091</td><td>$\mu_1 = -0{\cdot}798$</td></tr>
<tr><td></td><td>$b_2 = 1{\cdot}991$</td><td>0·0409</td><td>0·9991</td><td>−0·0110</td><td>$\mu_2 = 0{\cdot}763$</td></tr>
<tr><td></td><td>$b_3 = 1{\cdot}241$</td><td>−0·0086</td><td>0·0114</td><td>0·9999</td><td>$\mu_3 = -0{\cdot}362$</td></tr>
<tr><td colspan="6">whence $10^{35}\theta_1 = 12{\cdot}22$, $10^{35}\theta_2 = 12{\cdot}51$, and $10^{12}{}_{\rm m}K$ calc. = 104; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 10{\cdot}41$, $10^{35}\theta_2 = 11{\cdot}53$, and $10^{12}{}_{\rm m}K$ calc. = 92·3.</td></tr>
</table>

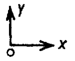
$C_{Ar}OMe$ triangle of A is rotated about C–O by 17°; and E, in which the $C_{Ar}OMe$ triangle of B is similarly rotated by 19°. "Division of ΔB" means distribution over b_1 and b_2 in the ratio $\cos^2 30° : \sin^2 30°$. The measured ${}_{\rm m}K$ is $70{\cdot}9 \times 10^{-12}$. Neither of the planar forms, A and B, nor the form C, alone corresponds with observations. If a single (or average) conformation is to be specified therefore, the high positivities of the ${}_{\rm m}K$'s calc. for A and B, and the negativity of that for C, point to a non-planar version of either A or B. "Trial and error" computations (illustrated by the data for D in Table 8) show one possibility starting from A; they are presented because the angle 17° is of the order of those deduced in anisole and 1-methoxynaphthalene. With B an angle greater than 19° (cf. E in Table 8) is required to reduce the ${}_{\rm m}K$ calc. to that observed. A unique decision cannot be made; 2-methoxynaphthalene lacks the argument from steric hindrance available for its 1-isomer; our measurements would be equally explicable if the 2-methoxy-derivative were a mixture of non-planar forms based on A and B.

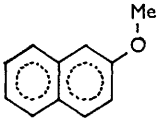


(IA)

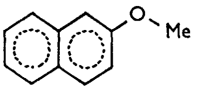


(IB)





(IIA)



(IIB)

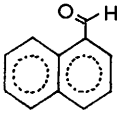
Scale drawings of the two extreme planar forms of 1-naphthaldehyde (IIIA and B) suggest that (IIIB) is sterically much less hindered than (IIIA) which involves considerable overlap between the van der Waals radii of the carbonyl oxygen and the 8-hydrogen atom.

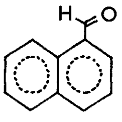
TABLE 9.

Principal polarisabilities, moment components, etc., calculated for 1-naphthaldehyde.

Model		Direction cosines with			
		OX	*OY*	*OZ*	
A or B (planar)	$b_1 = 2{\cdot}389$	0·9995	0·0314	0	$\mu_1 = 2{\cdot}529$
	$b_2 = 2{\cdot}017$	−0·0314	0·9995	0	$\mu_2 = 1{\cdot}356$
	$b_3 = 1{\cdot}104$	0	0	1	$\mu_3 = 0$
whence $10^{35}\theta_1 = 15{\cdot}59$, $10^{35}\theta_2 = 152{\cdot}23$, and $10^{12}{}_{\mathrm{m}}K$ calc. = 705·71; with Δb added to b_2, $10^{35}\theta_1 = 24{\cdot}53$, $10^{35}\theta_2 = 129{\cdot}48$, and $10^{12}{}_{\mathrm{m}}K$ calc. = 647·6.					
C (non-planar)	$b_1 = 2{\cdot}223$	1	0	0	$\mu_1 = 0$
	$b_2 = 2{\cdot}024$	0	0·9987	0·0506	$\mu_2 = 1{\cdot}559$
	$b_3 = 1{\cdot}263$	0	−0·0506	0·9987	$\mu_3 = 2{\cdot}410$
whence $10^{35}\theta_1 = 9{\cdot}15$, $10^{35}\theta_2 = -113{\cdot}30$, and $10^{12}{}_{\mathrm{m}}K$ calc. = −438; with Δb added to b_2, $10^{35}\theta_1 = 18{\cdot}23$, $10^{35}\theta_2 = -121{\cdot}24$, and $10^{12}{}_{\mathrm{m}}K$ calc. = −433.					
D (non-planar)	$b_1 = 2{\cdot}375$	0·9967	0·0690	0·0420	$\mu_1 = 2{\cdot}519$
	$b_2 = 2{\cdot}014$	−0·0702	0·9968	0·0389	$\mu_2 = 1{\cdot}247$
	$b_3 = 1{\cdot}130$	−0·0428	−0·0335	0·9986	$\mu_3 = 0{\cdot}589$
whence $10^{35}\theta_1 = 14{\cdot}63$, $10^{35}\theta_2 = 134{\cdot}78$, and $10^{12}{}_{\mathrm{m}}K$ calc. = 628; with Δb added to b_2, $10^{35}\theta_1 = 23{\cdot}43$, $10^{35}\theta_2 = 104{\cdot}78$, and $10^{12}{}_{\mathrm{m}}K$ calc. = 539.					

Relevant calculations are in Table 9. In conformation C the C_{Ar}·CHO unit is perpendicular to the naphthalene plane; in D this unit is rotated 15° from its position in (IIIA or B).


(IIIA)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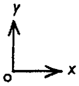
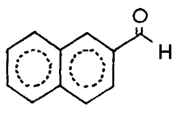


As a solute, therefore, 1-naphthaldehyde may exist as D; fully planar forms appear to be excluded.

With the 2-isomer the situation is different; steric considerations allow both (IVA) and (IVB) to be flat. Table 10 includes data for a form (IVC), in which the aldehyde and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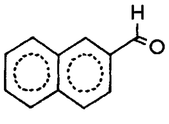

(IVB)

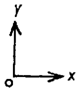


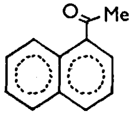
TABLE 10.

Principal polarisabilities, moment components, etc., calculated for 2-naphthaldehyde.

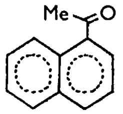
Model		Direction cosines with			
		OX	*OY*	*OZ*	
A (planar)	$b_1 = 2{\cdot}374$	0·9997	0·0262	0	$\mu_1 = 0{\cdot}08$
	$b_2 = 2{\cdot}032$	−0·0262	0·9997	0	$\mu_2 = 3{\cdot}139$
	$b_3 = 1{\cdot}104$	0	0	1	$\mu_3 = 0$
whence $10^{35}\theta_1 = 15{\cdot}40$, $10^{35}\theta_2 = 75{\cdot}95$, and $10^{12}{}_{\mathrm{m}}K$ calc. = 384; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 24{\cdot}73$, $10^{35}\theta_2 = 59{\cdot}96$, and $10^{12}{}_{\mathrm{m}}K$ = 356.					
B (planar)	$b_1 = 2{\cdot}438_2$	0·9998	−0·0175	0	$\mu_1 = 2{\cdot}746$
	$b_2 = 1{\cdot}967_8$	0·0175	0·9998	0	$\mu_2 = -1{\cdot}522$
	$b_3 = 1{\cdot}104$	0	0	1	$\mu_3 = 0$
whence $10^{35}\theta_1 = 16{\cdot}33$, $10^{35}\theta_2 = 190{\cdot}63$, and $10^{12}{}_{\mathrm{m}}K$ calc. = 870; with Δb divided between b_1 and b_2. $10^{35}\theta_1 = 26{\cdot}22$, $10^{35}\theta_2 = 248{\cdot}54$, and $10^{12}{}_{\mathrm{m}}K$ calc. = 1155.					
C (non-planar)	$b_1 = 2{\cdot}379$	0·9863	0·1618	0·0327	$\mu_1 = 1{\cdot}626$
	$b_2 = 1{\cdot}867$	−0·1626	0·9864	0·0228	$\mu_2 = 0{\cdot}379$
	$b_3 = 1{\cdot}264$	−0·0286	−0·0278	0·9992	$\mu_3 = 2{\cdot}660$
whence $10^{35}\theta_1 = 11{\cdot}11$, $10^{35}\theta_2 = -118{\cdot}11$, and $10^{12}{}_{\mathrm{m}}K$ calc. = −450; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 19{\cdot}19$, $10^{35}\theta_2 = -121{\cdot}58$, and $10^{12}{}_{\mathrm{m}}K$ calc. = −431.					

the naphthyl plane are mutually perpendicular; this, however, cannot exist in appreciable amounts since the observed molar Kerr constant is positive ($+1235 \times 10^{-12}$). The choice lies between forms A and B; the latter is obviously preferable as its ${}_{\mathrm{m}}K$ calc. is nearer ${}_{\mathrm{m}}K$ found, although *ca.* 8% too low. Perhaps the exaltation of polarisability should be preponderantly applied to b_1 (even when it is wholly so added, ${}_{\mathrm{m}}K$ calc. becomes only 1279×10^{-12}); at any rate there is no strong case for supposing non-planar conformations.

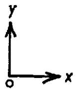
Leybold models suggest that either planar form (VA or B) of 1-acetylnaphthalene will be subject to steric hindrances between the carbonyl-oxygen atom or the methyl group and the *peri*-hydrogen of the naphthalene nucleus, but that the hindrance in (VA) is probably less than in (VB). Relevant calculations are in Table 11. Model C has the C_{Ar}–CO·Me unit lying at 90° to the $C_{10}H_7$ plane; in D (derived from A) the corresponding angle is 30·5°. The molar Kerr constants predicted for forms A, B, and C are either excessively positive or negative. A conformation such as D is appropriate (${}_{\mathrm{m}}K$ calc. = 345; obs. = 341×10^{-12}).



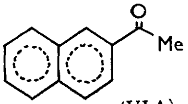
(VA)



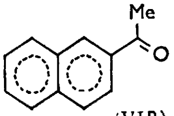
(VB)



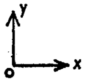
With 2-acetylnaphthalene the flat structures (VIA and B) seem equally possible from models. Calculations (Table 12), however, strongly favour (VIB), the ${}_{\mathrm{m}}K$ calc. for which is 911×10^{-12} (against the measured value of 952×10^{-12}). Non-planar variants of (VIA or B) would have lower ${}_{\mathrm{m}}K$'s (illustrated by the highly negative ${}_{\mathrm{m}}K$ forecast for the orthogonal conformation C).



(VIA)



(VIB)



A point of possible relevance to 2-naphthaldehyde and 2-acetylnaphthalene is that in the parent hydrocarbon the 1,2-carbon–carbon bond is the shortest in the molecule (M 224 of ref. 29 gives it as 1·35—1·36 Å); it therefore has the greatest double-bond character and

TABLE 11.

Principal polarisabilities, moment components, etc., calculated for 1-acetylnaphthalene.

Model		Direction cosines with			
		OX	*OY*	*OZ*	
A or B (planar)	$b_1 = 2{\cdot}593_8$	$0{\cdot}9998_5$	$0{\cdot}0174_5$	0	$\mu_1 = 2{\cdot}52_8$
	$b_2 = 2{\cdot}194_2$	$-0{\cdot}0174_5$	$0{\cdot}9998_5$	0	$\mu_2 = 1{\cdot}401$
	$b_3 = 1{\cdot}259$	0	0	1	$\mu_3 = 0$

whence $10^{35}\theta_1 = 16{\cdot}74$, $10^{35}\theta_2 = 159{\cdot}34$, and $10^{12}{}_{\mathrm{m}}K$ calc. = 740; with Δb added to b_2, $10^{35}\theta_1 = 19{\cdot}07$, $10^{35}\theta_2 = 151{\cdot}25$, and $10^{12}{}_{\mathrm{m}}K$ calc. = 716.

C (non-planar)	$b_1 = 2{\cdot}379$	1	0	0	$\mu_1 = 0$
	$b_2 = 2{\cdot}194_3$	0	0·9999	0·0105	$\mu_2 = 1{\cdot}467$
	$b_3 = 1{\cdot}473_7$	0	−0·0105	0·9999	$\mu_3 = 2{\cdot}490$

whence $10^{35}\theta_1 = 8{\cdot}15$, $10^{35}\theta_2 = -117{\cdot}22$, and $10^{12}{}_{\mathrm{m}}K$ calc. = −459; with Δb added to b_2, $10^{35}\theta_1 = 10{\cdot}48$, $10^{35}\theta_2 = -128{\cdot}97$, and $10^{12}{}_{\mathrm{m}}K$ calc. = −498.

D (non-planar)	$b_1 = 2{\cdot}553$	0·9929	0·0921	0·0742	$\mu_1 = 2{\cdot}284$
	$b_2 = 2{\cdot}175$	−0·0931	0·9958	0·0042	$\mu_2 = 1{\cdot}255$
	$b_3 = 1{\cdot}318$	−0·0732	−0·0051	0·9973	$\mu_3 = 1{\cdot}249$

whence $10^{35}\theta_1 = 14{\cdot}28$, $10^{35}\theta_2 = 70{\cdot}82$, and $10^{12}{}_{\mathrm{m}}K = 358$; with Δb added to b_2, $10^{35}\theta_1 = 16{\cdot}44$, $10^{35}\theta_2 = 65{\cdot}65$, and $10^{12}{}_{\mathrm{m}}K$ calc. = 345.

TABLE 12.

Principal polarisabilities, moment components, etc., calculated for 2-acetylnaphthalene.

Model		Direction cosines with *OX*	*OY*	*OZ*	
A (planar)	$b_1 = 2{\cdot}580$	1	0	0	$\mu_1 = 0$
	$b_2 = 2{\cdot}208$	0	1	0	$\mu_2 = 3{\cdot}18$
	$b_3 = 1{\cdot}259$	0	0	1	$\mu_3 = 0$

whence $10^{35}\theta_1 = 16{\cdot}55$, $10^{35}\theta_2 = 76{\cdot}80$, and $10^{12}{}_{\mathrm{m}}K = 392{\cdot}5$; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 17{\cdot}44$, $10^{35}\theta_2 = 74{\cdot}87$, and $10^{12}{}_{\mathrm{m}}K = 388$.

B (planar)	$b_1 = 2{\cdot}593_7$	$0{\cdot}9998_5$	$-0{\cdot}0174_5$	0	$\mu_1 = 2{\cdot}781$
	$b_2 = 2{\cdot}194_3$	$0{\cdot}0174_5$	$0{\cdot}9998_5$	0	$\mu_2 = 1{\cdot}542$
	$b_3 = 1{\cdot}259$	0	0	1	$\mu_3 = 0$

whence $10^{35}\theta_1 = 16{\cdot}73$, $10^{35}\theta_2 = 192{\cdot}83$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= 881{\cdot}2$; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 17{\cdot}64$, $10^{35}\theta_2 = 199{\cdot}02$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= 911$.

C (non-planar)	$b_1 = 2{\cdot}548_7$	$0{\cdot}9849_7$	$0{\cdot}1726$	$0{\cdot}0069$	$\mu_1 = 1{\cdot}584$
	$b_2 = 2{\cdot}024_3$	$-0{\cdot}1726$	$0{\cdot}9849_8$	$0{\cdot}0048$	$\mu_2 = 0{\cdot}291$
	$b_3 = 1{\cdot}4740$	$-0{\cdot}0059$	$-0{\cdot}0059$	$0{\cdot}9999_7$	$\mu_3 = 2{\cdot}742$

whence $10^{35}\theta_1 = 10{\cdot}30$, $10^{35}\theta_2 = -107{\cdot}72$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= -410$; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 11{\cdot}06$, $10^{35}\theta_2 = -110{\cdot}73$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= -419$.

will conjugate most stably with a side chain carrying a double bond when the latter is disposed *trans* to the 1,2-link in the $C_{10}H_7$ group. Thus the preferred conformations just described can be understood.

When the polarisabilities recorded by Le Fèvre and Rao [27] for the C_{Ar}–CN unit in benzonitrile are used, computations for 1- and 2-naphthonitrile appear as in Table 13. The calculated molar Kerr constants for these nitriles are 4% too high and 20% too low for the 1- and the 2-isomer, respectively. No explanation is obvious, unless greater conjugation occurs between C≡N and naphthyl than between C≡N and phenyl (compare the views expressed by Sauret and Lalande [33] regarding the differences between the measured and the calculated magnetic susceptibilities of the naphthonitriles) in which case the appropriateness of data from benzonitrile is to be questioned. In each molecule, $\mu_{\text{resultant}}$ is taken as parallel to the C–C≡N line; this neglects the transannular component [34] which in both structures will tend to produce resultants rotated somewhat from the C–C≡N directions towards the *OX*-axis. In such circumstances a slightly greater anisotropy (cf. remarks above, and ref. 33) for the C–C≡N unit can be envisaged, and the prediction can be improved for 2-naphthonitrile without impairing that for 1-naphthonitrile. It is suggestive that, even with the values in the lower half of Table 13, if $\mu_{\text{resultant}}$ and b_1 are collinear,

TABLE 13.

Principal polarisabilities, moment components, etc., calculated for 1- and 2-naphthonitrile.

1-$C_{10}H_7$·CN (planar)

	Direction cosines with * *OX*	*OY*	*OZ*	
$b_1 = 2{\cdot}196$	1	0	0	$\mu_1 = 0$
$b_2 = 2{\cdot}266$	0	1	0	$\mu_2 = 3{\cdot}99$
$b_3 = 1{\cdot}111$	0	0	1	$\mu_3 = 0$

whence $10^{35}\theta_1 = 14{\cdot}95$, $10^{35}\theta_2 = 256{\cdot}0$, and $10^{12}{}_{\mathrm{m}}K = 1140$; with Δb added to b_2, $10^{35}\theta_1 = 14{\cdot}61$, $10^{35}\theta_2 = 246{\cdot}0$, and $10^{12}{}_{\mathrm{m}}K = 1096$.

2-$C_{10}H_7$·CN (planar)

	Direction cosines with * *OX*	*OY*	*OZ*	
$b_1 = 2{\cdot}600$	$0{\cdot}9719$	$0{\cdot}2357$	0	$\mu_1 = 4{\cdot}14$
$b_2 = 1{\cdot}863$	$-0{\cdot}2357$	$0{\cdot}9719$	0	$\mu_2 = 1{\cdot}22$
$b_3 = 1{\cdot}111$	0	0	1	$\mu_3 = 0$

whence $10^{35}\theta_1 = 19{\cdot}79$, $10^{35}\theta_2 = 502{\cdot}2$, and $10^{12}{}_{\mathrm{m}}K = 2195$; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 22{\cdot}45$, $10^{35}\theta_2 = 538{\cdot}3$, and $10^{12}{}_{\mathrm{m}}K = 2358$.

* *OX* and *OY* are in the $C_{10}H_7$ plane, with *OY* parallel to the central bond in the naphthyl group.

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[33] Sauret and Lalande, *Compt. rend.*, 1953, **236**, 2066.

[34] Hampson and Weissberger, *J.*, 1936, 393.

and Δb is applied wholly to b_1, the ${}_{\mathrm{m}}K$ calc. emerges as 2662×10^{-12}, *i.e.*, only 10% in error.

Table 14 summarises predictions for 1- and 2-nitronaphthalene, in which the Le Fèvre–Rao [27] polarisabilities of C_{Ar}–NO_2 (from nitrobenzene) have been incorporated. As with the nitriles, the ${}_{\mathrm{m}}K$'s calculated for the 1- and 2-derivative are, respectively, higher and lower than the ${}_{\mathrm{m}}K$'s in Table 3. Here, however, models (or scale drawings) based on van der Waals atomic radii clearly suggest that a 1-nitro-group cannot be co-planar with the $C_{10}H_7$ ring although for a 2-nitro-group this is possible. In the 1-isomer only, therefore, "steric inhibition of resonance" is to be expected, and the anisotropy of the C_{Ar}–NO_2 bond should be expected to be less than in nitrobenzene (probably a little modified towards that found in nitromethane [27]); qualitatively both such diminished anisotropy and non-planarity should reduce the molar Kerr constant. (A deflection of C_{Ar}–NO_2 in the *XOY* plane, as suggested for 1,5-dinitronaphthalene in M 223 of ref. 29 would also tend to reduce ${}_{\mathrm{m}}K$ calc., but energetically rotation is preferable to distortion. Moreover, the details in M 223 are annotated as subject to uncertain errors and to a planar molecule's being assumed.) A slightly greater resonance in 2-nitronaphthalene than in nitrobenzene will, of course, increase the anisotropy of C_{Ar}–NO_2 and conduce to an elevation of ${}_{\mathrm{m}}K$ obs., in harmony with the facts.

TABLE 14.

Principal polarisabilities, moment components, etc., calculated for 1- and 2-nitronaphthalene.

1-$C_{10}H_7 \cdot NO_2$ (planar)

	Direction cosines with *			
	OX	*OY*	*OZ*	
$b_1 = 2{\cdot}236$	1	0	0	$\mu_1 = 0$
$b_2 = 2{\cdot}266$	0	1	0	$\mu_2 = 3{\cdot}98$
$b_3 = 1{\cdot}156$	0	0	1	$\mu_3 = 0$

whence $10^{35}\theta_1 = 14{\cdot}26$, $10^{35}\theta_2 = 237{\cdot}1$, and $10^{12}{}_{\mathrm{m}}K = 1057$; with Δb added to b_2, $10^{35}\theta_1 = 19{\cdot}08$, $10^{35}\theta_2 = 355{\cdot}6$, and $10^{12}{}_{\mathrm{m}}K = 1576$.

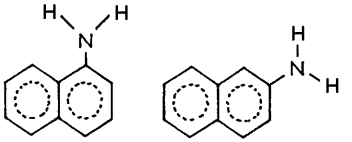
2-$C_{10}H_7 \cdot NO_2$ (planar)

	Direction cosines with *			
	OX	*OY*	*OZ*	
$b_1 = 2{\cdot}604$	0·9627	0·2706	0	$\mu_1 = 4{\cdot}254$
$b_2 = 1{\cdot}899$	−0·2706	0·9627	0	$\mu_2 = 1{\cdot}084$
$b_3 = 1{\cdot}156$	0	0	1	$\mu_3 = 0$

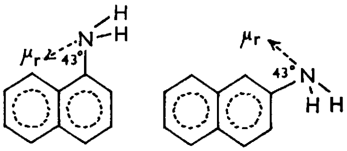
whence $10^{35}\theta_1 = 18{\cdot}69$, $10^{35}\theta_2 = 512{\cdot}3$, and $10^{12}{}_{\mathrm{m}}K = 2233$; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 25{\cdot}43$, $10^{35}\theta_2 = 606{\cdot}54$, and $10^{12}{}_{\mathrm{m}}K = 2658$.

* Cf. footnote to Table 13.

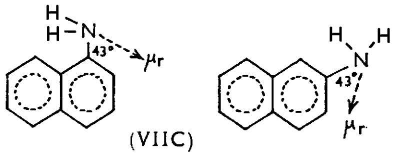
Finally, we consider the cases of 1- and 2-naphthylamine, the ${}_{\mathrm{m}}K$'s for which (like that of aniline in the unimolecular state, examined by Aroney and Le Fèvre [9] in 1956) are algebraically positive. As the amino-group can theoretically be rotated about the C_{Ar}–N bond the naphthylamines might, *a priori*, assume an infinite number of conformations between three extremes indicated by (VIIA, B, and C). In the A forms the line joining the amino-hydrogen atoms is parallel to the plane of the naphthalene ring; in the B and



(VIIA)



(VIIB)



(VIIC)

the C form it is perpendicular. The angles C–N–H and H–N–H are taken[35] as 109°. For the calculations given in Table 15 we have used bond polarisability ellipsoids from ref. 9*b* and followed Marsden and Sutton[36] by setting $\mu_{\text{resultant}}$ as acting at 43° to the C–N direction and in the plane defined by the C–N longitudinal axis and the bisector of the H–N–H angle. Intermediate conformations D are defined beneath Table 15. For 1-naphthylamine the forms B and C cannot be distinguished by their *b*'s, μ's, or ${}_{\mathrm{m}}K$'s, but for the 2-isomer the moment components and hence the ${}_{\mathrm{m}}K$'s are different.

TABLE 15.

Principal polarisabilities, moment components, etc., calculated for 1- and 2-naphthylamine.

Form		Direction cosines with * *OX*	*OY*	*OZ*	
		1-Naphthylamine			
A	$b_1 = 2{\cdot}277$	1	0	0	$\mu_1 = 0$
	$b_2 = 1{\cdot}904_1$	0	$0{\cdot}9999_5$	$-0{\cdot}0104_7$	$\mu_2 = 1{\cdot}100$
	$b_3 = 1{\cdot}193_9$	0	0·01047	$0{\cdot}9999_5$	$\mu_3 = 1{\cdot}005$

whence $10^{35}\theta_1 = 10{\cdot}79$, $10^{35}\theta_2 = -18{\cdot}42$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= -32{\cdot}1$; with Δb added to b_2, $10^{35}\theta_1 = 11{\cdot}61$, $10^{35}\theta_2 = -15{\cdot}78$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= -17{\cdot}54$.

B or C	$b_1 = 2{\cdot}305_1$	$0{\cdot}9999_5$	0·01047	0	$\mu_1 = 1{\cdot}028$
	$b_2 = 1{\cdot}913_9$	−0·01047	$0{\cdot}9999_5$	0	$\mu_2 = 1{\cdot}079$
	$b_3 = 1{\cdot}157$	0	0	1	$\mu_3 = 0$

whence $10^{35}\theta_1 = 12{\cdot}14$, $10^{35}\theta_2 = 26{\cdot}95$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= 164{\cdot}4$; with Δb added to b_2, $10^{35}\theta_1 = 13{\cdot}01$, $10^{35}\theta_2 = 27{\cdot}19$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= 169$.

D †	$b_1 = 2{\cdot}296$	0·9995	0·0300	0·0112	$\mu_1 = 0{\cdot}713$
	$b_2 = 1{\cdot}911$	−0·0291	0·9996	−0·0054	$\mu_2 = 1{\cdot}114$
	$b_3 = 1{\cdot}169$	−0·0110	0·0058	0·9999	$\mu_3 = 0{\cdot}686$

whence $10^{35}\theta_1 = 11{\cdot}70$, $10^{35}\theta_2 = 3{\cdot}25$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= 62{\cdot}9$; with Δb added to b_2, $10^{35}\theta_1 = 12{\cdot}55$, $10^{35}\theta_2 = 7{\cdot}13$, and $10^{12}{}_{\mathrm{m}}K = 82{\cdot}7_6$.

		2-Naphthylamine			
A	$b_1 = 2{\cdot}290_2$	$0{\cdot}9997_8$	$0{\cdot}0191_8$	$0{\cdot}0080_2$	$\mu_1 = 1{\cdot}150$
	$b_2 = 1{\cdot}891_9$	$-0{\cdot}0192_4$	$0{\cdot}9997_9$	$0{\cdot}0070_7$	$\mu_2 = 0{\cdot}638$
	$b_3 = 1{\cdot}193_9$	$-0{\cdot}0078_9$	$-0{\cdot}0072_2$	$0{\cdot}9999_4$	$\mu_3 = 1{\cdot}200$

whence $10^{35}\theta_1 = 10{\cdot}98$, $10^{35}\theta_2 = -6{\cdot}37$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= 19{\cdot}39$; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 11{\cdot}91$, $10^{35}\theta_2 = -6{\cdot}28$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= 23{\cdot}68$.

B	$b_1 = 2{\cdot}296$	1	0	0	$\mu_1 = 1{\cdot}734$
	$b_2 = 1{\cdot}922$	0	1	0	$\mu_2 = 0{\cdot}401$
	$b_3 = 1{\cdot}157$	0	0	1	$\mu_3 = 0$

whence $10^{35}\theta_1 = 12{\cdot}02$, $10^{35}\theta_2 = 60{\cdot}56$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= 305{\cdot}2$; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 13{\cdot}00$, $10^{35}\theta_2 = 63{\cdot}73$, and $10^{12}{}_{\mathrm{m}}K$ calc. $= 322{\cdot}7$.

C	$b_1 = 2{\cdot}312$	1	0	0	$\mu_1 = 0{\cdot}520$
	$b_2 = 1{\cdot}906$	0	1	0	$\mu_2 = 1{\cdot}702$
	$b_3 = 1{\cdot}157$	0	0	1	$\mu_3 = 0$

whence $10^{35}\theta_1 = 12{\cdot}24$, $10^{35}\theta_2 = 18{\cdot}58$, and $10^{12}{}_{\mathrm{m}}K = 129{\cdot}6$; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 13{\cdot}2_2$, $10^{35}\theta_2 = 18{\cdot}26$, and $10^{12}{}_{\mathrm{m}}K = 132{\cdot}4$.

D ‡	$b_1 = 2{\cdot}295$	0·9995	0·0315	0·0016	$\mu_1 = -0{\cdot}732$
	$b_2 = 1{\cdot}913$	−0·0315	0·9994	−0·0173	$\mu_2 = -1{\cdot}405$
	$b_3 = 1{\cdot}168$	−0·0022	0·0173	0·9998	$\mu_3 = 0{\cdot}812$

whence $10^{35}\theta_1 = 11{\cdot}71$, $10^{35}\theta_2 = 3{\cdot}83$, and $10^{12}{}_{\mathrm{m}}K = 65{\cdot}3_5$; with Δb divided between b_1 and b_2, $10^{35}\theta_1 = 12{\cdot}66$, $10^{35}\theta_2 = 3{\cdot}42$, and $10^{12}{}_{\mathrm{m}}K = 67{\cdot}6_2$.

* See footnote to Table 13. † C–NH_2 unit twisted about C–N by 28° from its position in the immediately preceding form B. ‡ C–NH_2 unit twisted about C–N by 28° from its position in the immediately preceding form C.

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[35] Brockway and Jenkins, *J. Amer. Chem. Soc.*, 1936, **58**, 2036; Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945.

[36] Marsden and Sutton, *J.*, 1936, 599.

With 1-naphthylamine the $_mK$'s forecast for A or B, and for C, are negative or highly positive, respectively; the observed value lies between these limits. By trial and error the 28° twisted conformation D is found to be satisfactory. With 2-naphthylamine, of the first three extremes, C most nearly agrees with experiment, although again prediction is greatly improved by supposing a 28° twist. Leybold models reveal steric interference between the *peri*- and the amino-hydrogen atoms in the 1-isomer; this could account for the rotation of the amino-group. No such hindrance, however, can be discerned in 2-naphthylamine. The D forms are, therefore, advanced as specifiable equivalent structures capable of explaining the measurements but not necessarily representing all solute molecules uniformly; obviously mixtures of A with B or C could be devised which would be just as harmonious with observations.

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