665. *Molecular Polarisability. A Study of Internal Rotation in the Benzyl Halides and Related Molecules from Measurements of Molar Kerr Constants and Dipole Moments*

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Molar Kerr constants and apparent dipole moments are recorded for benzyl chloride, benzyl bromide, benzyl iodide, 1-chloromethylnaphthalene, 4-chlorobenzyl chloride, 4-bromobenzyl bromide, and benzyl cyanide as solutes in carbon tetrachloride at 25°. The dependence of the molar Kerr constants on molecular conformation is considered, and the results discussed in relation to internal rotation in the molecules. For the first four compounds, the potential-energy function governing internal rotation is estimated from van der Waals interaction data, and average molar Kerr constants calculated therefrom.

This Paper deals with the problem of internal rotation in a number of aromatic molecules containing the CH_2X substituent group (where X = halogen or CN), by the approach recently adopted for 1,2-dichloroethane.[1] Molar Kerr constants and dipole moments, measured in carbon tetrachloride at 25°, for seven such compounds are recorded in Tables 1 and 2. The results are then discussed in relation to factors influencing internal rotation of the CH_2X group in these molecules.

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[1] R. J. W. Le Fèvre and B. J. Orr, *Austral. J. Chem.*, 1964, **17**, 1098.

TABLE 1

Incremental Kerr effects, dielectric constants, etc., for solutions in carbon tetrachloride at 25°

Benzyl chloride

$10^5 w_2$	2039	2574	4116	4539	6423	6990	
$10^4 \Delta\varepsilon$	1085	1370	2187	2394	3386	3702	
$10^5 w_2$	2039	3458	4116	5651	5683	7819	
$-10^4 \Delta d$	137	237	280	385	381	529	
$10^5 w_2$	2924	4539	4588	6990			
$10^4 \Delta n$	38	57	56	86			
$10^5 w_2$	1506	1864	3196	3453	5633	6534	7509
$10^{11} \Delta B$	88	118	175	216	340	401	438

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 5{\cdot}29$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}68$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}124$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}36$; $\Sigma\Delta B/\Sigma w_2 = 0{\cdot}60 \times 10^{-7}$

Benzyl bromide

$10^5 w_2$	1792	2752	3552	4628	5001	6659
$10^4 \Delta\varepsilon$	727	1115	1442	1895	2047	2735
$-10^5 \Delta d$	281	359	596	682	703	976
$10^4 \Delta n$	25	39	50	64	70	91
$10^{11} \Delta B$	302	605	837	1042	1042	1364

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 4{\cdot}08$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}15$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}139$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}41$; $\Sigma\Delta B/\Sigma w_2 = 2{\cdot}13 \times 10^{-7}$

Benzyl iodide

$10^5 w_2$	1126	2221	3166	4080	5245	6455
$10^4 \Delta\varepsilon$	309	616	882	1138	1466	1814
$10^5 \Delta d$	138	348	474	576	825	964
$10^4 \Delta n$	19	38	53	68	89	108
$10^{11} \Delta B$	486	935	1276	1677	2232	2841

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}79$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}15$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}168$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}49$; $\Sigma\Delta B/\Sigma w_2 = 4{\cdot}24 \times 10^{-7}$

1-*Chloromethylnaphthalene*

$10^5 w_2$	1459	3025	4021	4906
$10^4 \Delta\varepsilon$	553	1378	1846	2240
$-10^5 \Delta d$	789	1489	2023	2446
$10^4 \Delta n$	39	79	111	132
$-10^{11} \Delta B$	465	1244	1677	2189

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 4{\cdot}49$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}50$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}269$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}79$; $\Sigma\Delta B/\Sigma w_2 = -4{\cdot}16 \times 10^{-7}$

4-*Chlorobenzyl chloride*

$10^5 w_2$	479	671	921	1061	1466	1903
$10^4 \Delta\varepsilon$	179	254	347	401	555	722
$-10^5 \Delta d$	172	246	321	397	560	725
$10^4 \Delta n$	7	10	14	14	23	27
$10^5 w_2$	479	770	1061	1351	1466	1903
$-10^{11} \Delta B$	228	393	574	702	764	1002

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 3{\cdot}78$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}37$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}146$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}43$; $\Sigma\Delta B/\Sigma w_2 = -5{\cdot}21 \times 10^{-7}$

4-*Bromobenzyl bromide*

$10^5 w_2$	350	837	2297	2712	3016	4251
$10^4 \Delta\varepsilon$	84	214	590	681	771	1127
$10^5 \Delta d$	97	207	568	661	723	993
$10^4 \Delta n$	7	13	38	39	43	65
$-10^{11} \Delta B$	139	278	935	1116	1239	1805

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 2{\cdot}58$; $\Sigma\Delta d/\Sigma w_2 = 0{\cdot}24$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}15$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}46$; $\Sigma\Delta B/\Sigma w_2 = -4{\cdot}09 \times 10^{-7}$

Benzyl cyanide

$10^5 w_2$	212	380	511	723	970	1109
$10^4 \Delta\varepsilon$	415	754	1018	1434	1920	2194
$-10^5 \Delta d$	171	312	425	633	808	935
$10^4 \Delta n$	3	—	—	10	13	16
$10^{11} \Delta B$	436	774	1043	1438	1958	2196

whence $\Sigma\Delta\varepsilon/\Sigma w_2 = 19{\cdot}8$; $\Sigma\Delta d/\Sigma w_2 = -0{\cdot}84$; $\Sigma\Delta n/\Sigma w_2 = 0{\cdot}139$; $\Sigma\Delta n^2/\Sigma w_2 = 0{\cdot}41$; $\Sigma\Delta B/\Sigma w_2 = 20{\cdot}1 \times 10^{-7}$

TABLE 2

Polarisations, refractions, dipole moments, and molar Kerr constants in carbon tetrachloride

Solute	$\alpha\varepsilon_1$	β	$\gamma' n_1^2$	$_\infty P_2$ (c.c.)	R_D (c.c.)	μ (D) *	γ	δ	10^{12} $_\infty(_mK_2)$
$PhCH_2Cl$	5·29	−0·43	0·36	104·1	36·2	1·80	0·085	8·5	6·9
$PhCH_2Br$	4·08	−0·09	0·41	108·3	39·9	1·83	0·095	30·4	37·8
$PhCH_2I$	2·79	0·09	0·49	100·6	45·9	1·60	0·115	60·6	98·1
1-$C_{10}H_7CH_2Cl$...	4·49	−0·32	0·79	126·7	55·5	1·83	0·185	−59·4	−80·0
4-$ClC_6H_4CH_2Cl$	3·78	−0·23	0·43	100·9	41·9	1·67	0·100	−74·4	−94
4-$BrC_6H_4CH_2Br$	2·58	0·15	0·46	107·2	49·3	1·64	0·104	−58·4	−110
$PhCH_2CN$	19·8	−0·53	0·41	278·7	36·2	3·43	0·095	287	245

* It is assumed that $_DP = 1{\cdot}05\ R_D$.

EXPERIMENTAL

Materials.—Liquids were dried and redistilled immediately before use; drying agents and b. p.'s were: for benzyl chloride, sodium sulphate and 179°/760 mm.; for benzyl bromide, sodium sulphate and 130°/*ca*. 100 mm.; for 1-chloromethylnaphthalene (prepared as in ref. 2), potassium carbonate and 140°/10 mm.; for benzyl cyanide, sodium sulphate and 118°/25 mm. Benzyl iodide, prepared as in ref. 3, was recrystallised from ethanol at 0° and had m. p. 24°. 4-Chlorobenzyl chloride, fractionally crystallised, dried over phosphoric oxide, and redistilled at 180°/*ca*. 100 mm., had m. p. 27°. A commercial sample of 4-bromobenzyl bromide, with m. p. 64°, was used without further purification. Carbon tetrachloride, fractionated and dried over fused calcium chloride, was used throughout as solvent.

Apparatus.—Dielectric constants have been determined with apparatus as in ref. 4, associated procedures giving polarisations being standard.[5a] Kerr effects have been recorded photometrically with apparatus as in ref. 6.

Results.—These are listed in usual form in Tables 1 and 2. The symbols used are those previously explained in refs. 4, 5*a*, and 7*a*—*d*; they have recently been summarised in ref. 8.

Previous Measurements.—No previous dipole-moment measurements are on record for benzyl iodide, 1-chloromethylnaphthalene, or 4-bromobenzyl bromide; the apparent dipole moments of the remaining compounds of the series are in substantial agreement with those recorded in ref. 9. No previous measurements of $_\infty(_mK_2)$ for the compounds listed in Table 2 have been recorded.

DISCUSSION

Magnitude and Direction of Dipole Moments.—In estimating the directions in which the dipole moments of the molecules of this series act, it has been assumed that the observed moments (Table 2) are the resultants only of primary bond moments, and that the secondary effects of inductive and mesomeric moments may, for the present purposes, be neglected. It has further been assumed that all CCH and CCX bond angles in the C_{Ar}–CH_2X group are 110°. On this basis, the dipole moments of the benzyl halides, 1-chloromethylnaphthalene, and benzyl cyanide emerge as the resultant of a C–X bond moment and three C–H bond moments, tetrahedrally disposed. If the dipole moments of the C–H bonds in the CH_2X group and in the 4-position of the aromatic group are of the same order, the resultant dipole moment, $\mu_{res.}$, should act along the C–X bond axis.

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[2] A. I. Vogel, " Practical Organic Chemistry," Longmans, London, 3rd edn., 1959, p. 540.

[3] G. H. Coleman and C. R. Hauser, *J. Amer. Chem. Soc.*, 1928, **50**, 1196; 1929, **51**, 1497.

[4] A. D. Buckingham, J. Y. H. Chau, H. C. Freeman, R. J. W. Le Fèvre, D. A. A. S. Narayana Rao, and J. Tardif, *J.*, 1956, 1405.

[5] R. J. W. Le Fèvre, (*a*) " Dipole Moments," Methuen, London, 3rd edn., 1953, ch. 2; (*b*) *J. Proc. Roy. Soc. New South Wales*, 1961, **95**, 1.

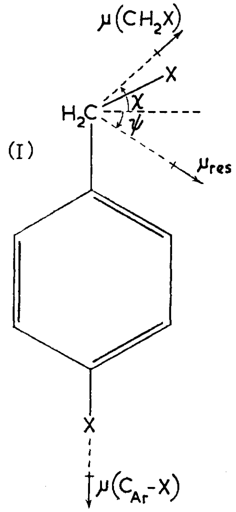
[6] R. J. W. Le Fèvre and G. L. D. Ritchie, *J.*, 1963, 4933.

[7] C. G. Le Fèvre and R. J. W. Le Fèvre, (*a*) *J.*, 1953, 4041; (*b*) *J.*, 1954, 1577; (*c*) *Rev. Pure Appl. Chem.* (*Australia*), 1955, **5**, 261; (*d*) in " Physical Methods of Organic Chemistry," ed. A. Weissberger, Interscience Publ. Inc., New York, 3rd edn., vol. I, p. 2459; (*e*) *J.*, 1955, 1641.

[8] R. J. W. Le Fèvre and K. M. S. Sundaram, *J.*, 1962, 1494.

[9] L. G. Wesson, " Tables of Electric Dipole Moments," Technology Press, M.I.T., 1948; A. L. McClellan, " Tables of Experimental Dipole Moments," Freeman and Co., San Francisco, 1963.

In the more complicated cases of 4-chlorobenzyl chloride and 4-bromobenzyl bromide, the dipole moment has been treated as the resultant of the moment, $\mu(C_{Ar}-X)$, of the *para*-substituent and of the moment, $\mu(CH_2X)$, of the CH_2X group. The magnitudes of $\mu(C_{Ar}-Cl)$ and $\mu(C_{Ar}-Br)$ are retained as 1·59 and 1·51 D, respectively, from the appropriate halogenobenzenes;[7b] likewise $\mu(CH_2Cl)$ and $\mu(CH_2Br)$ are adopted as 1·80 and 1·83 D, from the corresponding benzyl halides (Table 2). These data, together with the observed resultant moments, $\mu_{res.}$, permit the calculation of the directions of $\mu(CH_2X)$ and $\mu_{res.}$, defined respectively by angles χ and ψ, as in (I). For 4-chlorobenzyl chloride, $\chi = 31{\cdot}5°$ and $\psi = 23°$; for 4-bromobenzyl bromide, $\chi = 32°$ and $\psi = 19°$.



(I)

Molar Refractions.—Values of R_D (calc.) have been estimated for the molecules of the series by summation of the appropriate bond and group refractions given by Vogel,[10] no allowance being made for mesomeric or hyperconjugative effects due to the CH_2X group. The exaltation of refraction, ΔR_D, calculated as the difference between R_D (obs.) and R_D (calc.), gives an estimate of the double-bond character in the $C_{Ar}-C$ bond. Multiplication of ΔR_D by a factor of $(9/4\pi N)$, where N is the Avogadro number, yields the exaltation of polarisability, Δb, which, in ensuing calculations, has been assumed to be directed along the longitudinal axis of the $C_{Ar}-C$ bond. The results of such calculations are as in Table 3.

Dependence of ${}_mK$ on Molecular Conformation.—The various possible molecular conformations resulting from internal rotation about the $C_{Ar}-C$ bond may be designated by a parameter ϕ, which is the angle between the $C_{Ar}-C-X$ plane and the plane of the aromatic ring. For 1-chloromethylnaphthalene, we take $\phi = 0°$ when the chlorine atom is *cis*-oriented with respect to the 8-position of the α-naphthyl group, and $\phi = 180°$ when it is *trans*-oriented. For a number of values of ϕ, molecular polarisability semi-axes, b_1, b_2, b_3, have been estimated by addition of bond- and group-polarisability tensors and diagonalisation of the resulting matrices, following standard procedures.[5b,11] The bond- and group-polarisability semi-axes, b_L, b_T, b_V, used are given in Table 4. The b_L of the $C_{Ar}-C$ bond has been calculated as the sum of the usual b_L of the C–C bond and the Δb as in Table 3. Calculations have been performed with two sets of C–X bond-polarisabilities, obtained (i) from CH_3X, and (ii) from $(CH_3)_3CX$. The resultant molecular polarisabilities, in conjunction with the dipole-moment components, μ_1, μ_2, μ_3, along the axes of b_1, b_2, b_3, respectively, yield values of ${}_mK$ (calc.) as in Table 5.

TABLE 3

Molar refractions and exaltations of refraction and polarisability *

Molecule	$PhCH_2Cl$	$PhCH_2Br$	$PhCH_2I$	$1\text{-}C_{10}H_7CH_2Cl$	$4\text{-}ClC_6H_4CH_2Cl$	$4\text{-}BrC_6H_4CH_2Br$	$PhCH_2CN$
R_D (obs.)	36·2	39·9	45·9	55·5	41·9	49·3	36·2
R_D (calc.)	35·7	38·6	43·8	54·2	41·4	47·1	35·3
ΔR_D	+0·5	+1·3	+2·2	+1·4	+0·5	+2·2	+0·9
Δb	0·59	1·55	2·62	1·66	0·59	2·62	1·07

* Refractions are expressed in c.c. units; polarisabilities, here and elsewhere, are in cubic Ångström units (10^{-24} c.c.).

The values of ${}_mK$(calc.) for all the compounds have been found to satisfy closely a function of the form

$$10^{12}{}_mK(\phi) = a + b\cos 2\phi \qquad (1)$$

The parameters a and b, constants for a given molecule and choice of C–X bond polarisabilities, are listed, together with observed molar Kerr constants, ${}_mK$(obs.), in Table 6.

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[10] A. I. Vogel, *J.*, 1948, 654; A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J.*, 1952, 514.

[11] J. M. Eckert and R. J. W. Le Fèvre, *J.*, 1962, 1081.

Table 4

Assumed bond and group polarisability values

Bond or group	b_L	b_T	b_V	Bond or group environment	Ref.
C–H	0·64	0·64	0·64	Paraffins	5*b*
C–C	0·99	0·27	0·27	Cyclohexane	5*b*
C–Cl	3·2	2·2	2·2	CH_3Cl	5*b*
C–Cl	4·0	1·6	1·6	$(CH_3)_3CCl$	5*b*
C–Br	4·65	3·1	3·1	CH_3Br	5*b*
C–Br	6·0	2·6	2·6	$(CH_3)_3CBr$	5*b*
C–I	6·8	4·7	4·7	CH_3I	5*b*
C–I	9·2	3·7	3·7	$(CH_3)_3CI$	12*a*
C–CN	3·64	1·75	1·75	CH_3CN	12*b*
C–CN	4·03	1·54	1·54	$(CH_3)_3CCN$	12*b*
C_6H_5	10·56	10·56	6·72	C_6H_6	13
α-$C_{10}H_7$	20·86	16·96	9·66	$C_{10}H_8$	7*e*
4-ClC_6H_4	14·08	11·80	7·54	C_6H_5Cl	7*b*
4-BrC_6H_4	16·20	11·49	8·92	C_6H_5Br	7*b*

Table 5

Values of $10^{12}{}_{m}K$(calc.) for various conformations

	(i) b^{CX} as in CH_3X				(ii) b^{CX} as in $(CH_3)_3CX$			
$\phi°$	0	30	60	90	0	30	60	90
$PhCH_2Cl$	+102·2	+55·6	−38·1	−84·6	+156·5	+108·2	+11·0	−37·7
$PhCH_2Br$	+119·0	+70·0	−28·1	−77·2	+193·5	+142·1	+39·6	−11·9
$PhCH_2I$	+106·3	+67·6	−9·8	−48·2	+217·8	+175·1	+89·1	+46·2
1-$C_{10}H_7{\cdot}CH_2Cl$	+324·5	+183·8	−98·1	−239·3	+387·2	+241·0	−51·4	−197·4
4-$ClC_6H_4{\cdot}CH_2Cl$	+69·6	+26·7	−59·8	−102·5	+86·5	+41·7	−49·1	−93·9
4-$BrC_6H_4{\cdot}CH_2Br$	+20·7	−6·2	−60·3	−87·3	+44·7	+16·2	−41·1	−69·5
$PhCH_2{\cdot}CN$	+434·6	+267·1	−68·0	−236·0	+516·2	+348·3	+11·3	−156·5

Table 6

Coefficients of the function, ${}_{m}K(\phi) = a + b \cos 2\phi$

		(i) b^{CX} as in CH_3X		(ii) b^{CX} as in $(CH_3)_3CX$	
Molecule	$10^{12}{}_{m}K$ (obs.)	*a*	*b*	*a*	*b*
$PhCH_2Cl$	+6·9	8·7	93·4	59·5	97·1
$PhCH_2Br$	+37·8	20·9	98·1	90·8	102·5
$PhCH_2I$	+98·1	29·0	77·2	132·1	85·8
1-$C_{10}H_7{\cdot}CH_2Cl$	−80·0	42·7	281·9	94·8	292·2
4-$ClC_6H_4{\cdot}CH_2Cl$	−94	−16·4	86·0	−3·8	90·2
4-$BrC_6H_4{\cdot}CH_2Br$	−110	−33·3	54·0	−12·4	57·1
$PhCH_2{\cdot}CN$	+245	99·3	335·3	179·8	336·4

Comparison of ${}_{m}$K(obs.) *and* ${}_{m}$K (calc.).—The values of ${}_{m}K$ (calc.) are most simply compared with those of ${}_{m}K$ (obs.) by evaluation of the quantity $\langle\phi\rangle$; namely the ϕ, which for each set of conformations, satisfies the relation ${}_{m}K(\phi) = {}_{m}K$ (obs.). Such a parameter has been successfully employed in interpreting Kerr-effect results on numerous previous occasions (see, for example, refs. 14 and 15). Only in cases where molecular rigidity is to be expected, however, will $\langle\phi\rangle$ designate the actual molecular conformation; for more flexible molecules, nevertheless, values of $\langle\phi\rangle$ are sometimes useful in indicating trends in conformational distribution within a series.

Table 7 lists values of $\langle\phi\rangle$, estimated from the data of Table 6, for the members of the present series. Inspection of Table 7 reveals that expected trends in mean or effective conformation can in no way be associated with the trends in $\langle\phi\rangle$. Thus, for the three benzyl halides, $\langle\phi\rangle$ decreases with increasing molecular weight; this is contrary to expectations based on simple steric requirements. Likewise, the two 4-halogeno-compounds

[12] R. J. W. Le Fèvre, B. J. Orr, and G. L. D. Ritchie, (*a*) unpublished data; (*b*) *J.*, 1965, 2499.

[13] M. J. Aroney and R. J. W. Le Fèvre, *J.*, 1960, 3600.

[14] M. J. Aroney, R. J. W. Le Fèvre, and J. D. Saxby, *J.*, 1963, 1739; *Canad. J. Chem.*, 1964, **42**, 1493.

[15] M. J. Aroney, M. G. Corfield, and R. J. W. Le Fèvre, *J.*, 1964, 648.

TABLE 7

Values of $\langle\phi\rangle$ (in degrees)

Molecule	$PhCH_2Cl$	$PhCH_2Br$	$PhCH_2I$	$1\text{-}C_{10}H_7{\cdot}CH_2Cl$
(i) b^{CX} as in CH_3X	46	40	13	58
(ii) b^{CX} as in $(CH_3)_3CX$	62	60	56	64

Molecule	$4\text{-}ClC_6H_4{\cdot}CH_2Cl$	$4\text{-}BrC_6H_4{\cdot}CH_2Br$	$PhCH_2{\cdot}CN$
(i) b^{CX} as in CH_3X	77	*ca.* 90 *	32
(ii) b^{CX} as in $(CH_3)_3CX$	90	*ca.* 90 *	36

* For 4-bromobenzyl bromide, $_{m}K$ (obs.) is outside the range of values of $_{m}K$ (calc.)

yield results which deviate considerably from those for the remainder of the series. Furthermore, benzyl cyanide has an unexpectedly low value of $\langle\phi\rangle$. It can only be concluded, therefore, that evaluation of $\langle\phi\rangle$ is inadequate as a means of studying factors influencing internal rotation in the benzyl halide series.

A more realistic approach to the problem of internal rotation in this series involves the potential-energy function, $U(\phi)$, which determines the distribution amongst the various possible molecular conformations. The value $\langle_{m}K\rangle$, of the molar Kerr constant averaged over all conformations is given [1] by:

$$\langle_{m}K\rangle = \int_{-\pi}^{\pi} {}_{m}K(\phi)\exp[-U(\phi)/\boldsymbol{k}T]\mathrm{d}\phi \int_{-\pi}^{\pi} \exp[-U(\phi)/\boldsymbol{k}T]\mathrm{d}\phi, \tag{2}$$

where $\boldsymbol{k}$ and T are the Boltzmann constant and absolute temperature, respectively. It is possible to define an equivalent potential function of the form:

$$U(\phi) = v_0(1 + \cos 2\phi)/2, \tag{3}$$

where v_0 is the equivalent potential-energy barrier restricting internal rotation at $\phi = 0°$, and is chosen such that $\langle_{m}K\rangle = {}_{m}K(\text{obs.})$. The parameter v_0 is not to be identified [except when $U(\phi)$ is in fact of sinusoidal form] with the actual potential barrier at $\phi = 0°$; it might nevertheless be expected, in certain series of compounds, to indicate trends in their steric hindrance. Such a treatment can generally be successful, however, only if the sinusoidal function of equation (3) is a reasonably good approximation to the actual $U(\phi)$ of each member of the series.

Combination of equations 1—3 leads to the relation:

$$10^{12}\langle_{m}K\rangle = a + bL(v_0/2\boldsymbol{k}T), \tag{4}$$

where $L(v_0/2\boldsymbol{k}T)$ is the Langevin function in $v_0/2\boldsymbol{k}T$. Putting $\langle_{m}K\rangle = {}_{m}K$ (obs.), and with the data of Table 6, values of v_0 emerge as in Table 8.

TABLE 8

Values of equivalent potential-energy barrier, v_0 (in kcal./mole)

Molecule	$PhCH_2Cl$	$PhCH_2Br$	$PhCH_2I$	$1\text{-}C_{10}H_7{\cdot}CH_2Cl$
(i) b^{CX} as in CH_3X	+0·1	−0·6	−11·2	+1·8
(ii) b^{CX} as in $(CH_3)_3CX$	+2·4	+2·2	+1·6	+2·8

Molecule	$4\text{-}ClC_6H_4{\cdot}CH_2Cl$	$4\text{-}BrC_6H_4{\cdot}CH_2Br$	$PhCH_2{\cdot}CN$
(i) b^{CX} as in CH_3X	+12·1	$+\infty$ *	−1·8
(ii) b^{CX} as in $(CH_3)_3CX$	$+\infty$	$+\infty$ *	−1·1

* For 4-bromobenzyl bromide, $_{m}K$ (obs.) is outside the range of values of $_{m}K$ (calc.).

The values and trends of the parameter, v_0, of Table 8 are seen to be just as much in conflict with expectations as are the $\langle\phi\rangle$ values of Table 7. It must therefore be concluded that this approach, too, is inadequate as a means of studying internal rotation in these molecules. Consequently, such semi-empirical approaches as those involving $\langle\phi\rangle$ and v_0 have been abandoned, and theoretical calculations made of the actual potential function, $U(\phi)$. No further calculations have been performed for the two 4-halogeno-compounds owing to the apparently anomalous results of Tables 7 and 8, or for benzyl cyanide, for which insufficient data are available to permit calculation of $U(\phi)$.

Estimation of $U(\phi)$ and $\langle {}_{\mathrm{m}}K \rangle$.—For the benzyl halides and 1-chloromethylnaphthalene, an attempt has been made to obtain a better estimate of $U(\phi)$ than is provided by the equivalent potential function of equation (3). A consideration of molecular models suggests that it is reasonable to assume that van der Waals forces of attraction and repulsion predominate in determining $U(\phi)$ for these molecules, and that other effects (such as deformations of bond angles, torsional hindrances, dipole–dipole interactions, and solute–solvent interactions) may, for the present purposes, be neglected. Estimates of $U(\phi)$ have therefore been obtained from potential-energy functions for van der Waals interactions of a number of non-bonded pairs of atoms, by the methods in ref. 16. The functions are of the form:

$$U/\varepsilon = -2{\cdot}25\alpha^{-6} + 8{\cdot}28 \times 10^{5}\exp(-\alpha/0{\cdot}0736), \qquad (5)$$

where U is the potential energy for van der Waals interactions between two non-bonded atoms whose nuclei are separated by a distance α (expressed in units of the sum of their van der Waals radii), and ε is a constant which depends on the pair of atoms involved. Values of the constant ε for the interaction of hydrogen (bonded to carbon) with a number of atoms Y (bonded to carbon),[16] and of the van der Waals radius, R_{Y} for the atom Y [17] are listed in Table 9.

TABLE 9

Data for non-bonded interactions of H (to C) with Y (to C) [14,15]

Atom Y	H	Cl	Br	I
R_{Y} (Å)	1·20	1·80	1·95	2·15
ε (kcal./mole)	0·042	0·115	0·136	0·158

TABLE 10

Estimates of $U(\phi)$ (in kcal./mole) from van der Waals interactions

Benzyl chloride

ϕ	0	10	20	30	40	50	60	70	80	90
$U(\phi)$	1·36	1·18	0·80	0·42	0·16	0·04	0·01	0·00	0·00	0·01

Benzyl bromide

ϕ	0	10	20	30	40	50	60	70	80	90
$U(\phi)$	2·55	2·25	1·52	0·81	0·33	0·10	0·02	0·00	0·00	0·00

Benzyl iodide

ϕ	0	10	20	30	40	50	60	70	80	90
$U(\phi)$	4·86	4·28	2·94	1·61	0·70	0·23	0·06	0·01	0·00	0·00

1-*Chloromethylnaphthalene*

ϕ	0	10	20	30	40	50	60	70	80	90
$U(\phi)$	236·6	191·4	105·7	43·8	14·6	4·02	0·79	0·01	0·06	0·58
ϕ	100	110	120	130	140	150	160	170	180	
$U(\phi)$	1·48	2·45	2·88	2·50	1·65	1·01	0·85	0·96	1·07	

For the benzyl halides, the values of $U(\phi)$ have been estimated for a number of values of ϕ as the sum of the separate interaction energies, U, for the atom X and the two protons of the CH_2X group with both *ortho* protons of the phenyl group. This involves calculating the variation with ϕ of a number of interatomic distances and substituting, together with the data of Table 9, into equation (5). Average bond lengths [18] (in Å) assumed are: C–H = 1·101; C–Cl = 1·767; C–Br = 1·937; C–I = 2·135; C–C = 1·541; C_{Ar}–C_{Ar} = 1·395. A similar treatment for 1-chloromethylnaphthalene yields the interaction energies

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[16] T. L. Hill, *J. Chem. Phys.*, 1948, **16**, 399; N. L. Allinger, J. Allinger, L. A. Freiberg, R. F. Czaja, and N. A. Le Bel, *J. Amer. Chem. Soc.*, 1960, **82**, 5882.

[17] L. Pauling, " The Nature of the Chemical Bond," Cornell University Press, Ithaca, 2nd edn., 1940, p. 189.

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

of the chloromethyl group with the 2- and 8-protons of the naphthyl group. Values of the functions $U(\phi)$, adjusted such that their minimum values are zero, are as in Table 10.

Values of $\langle {}_{m}K \rangle$, estimated by substituting the results of Tables 6 and 10 into equation (2), are as in Table 11. The results have been calculated by evaluating, plotting, and graphically integrating the functions $\exp[-U(\phi)/kT]$ and ${}_{m}K(\phi)\exp[-U(\phi)/kT]$ between $\phi = 0°$ and $\phi = 180°$.

TABLE 11

Values of $\langle {}_{m}K \rangle$ calculated from $U(\phi)$

Molecule	$PhCH_2Cl$	$PhCH_2Br$	$PhCH_2I$	$1\text{-}C_{10}H_7\cdot CH_2Cl$
$10^{12}\langle {}_{m}K \rangle$ (i) b^{CX} as in CH_3X	−23·2	−26·2	−18·3	−94·7
$10^{12}\langle {}_{m}K \rangle$ (ii) b^{CX} as in $(CH_3)_3CX$	+26·0	+41·5	+80·3	−48·1
$10^{12}{}_{m}K$ (obs.)	+6·9	+37·8	+98·1	−80·0

Table 11 shows that the values of ${}_{m}K$ (obs.) for the four molecules are generally within the range of calculated values of $\langle {}_{m}K \rangle$ indicating that the experimental results are reasonably consistent with the figures for $U(\phi)$ in Table 10. Although trends in the appropriateness of b^{CX} are apparent, the nature of the approximations and assumptions inherent in the treatment do not justify any definite conclusions as to choice of bond polarisabilities, and direction of $\mu_{res.}$, or the previously neglected effects of bond-angle deformation, torsional hindrance, dipole–dipole interactions, and solute–solvent interactions.

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