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MOLECULAR REFRACTIVITY AND POLARIZABILITY

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I. INTRODUCTION

REFRACTIVE indices (n) of pure substances have been accurately measurable far longer than any other optical properties. The refractometers introduced by Abbe in 1874 and by Pulfrich in 1887 made easy and convenient the determination of n for a liquid to within five significant figures; interferometers, based on that described by Jamin in 1856, made possible higher precisions with liquids and have often been used to obtain the refractive indexes of gases and vapours. Details of these and other instruments in their modern forms, together with helpful operational instructions, and much information relevant generally to refraction, have been lately given by Bauer *et al.* (1960).

An unknown but certainly large number of refractive indices are scattered throughout the literature, particularly occurring in papers dealing with organic chemistry; their retrieval and collection into an up-to-date and complete list would today be an insuperable task. Fortunately, Beilstein's *Handbuch* usually includes refractive indices among the physical constants quoted under each compound heading. Compilations of older refractive indices are in the 5th edn. of Landolt-Börnstein's *Physikalisch-chemische Tabellen* (two vols. of which appeared in 1923, followed by six supplements during 1927–36) and in the 1st edn. of the *International Critical Tables* (issued in 1930); these two sources contain all the values available to Brühl, Eisenlohr, von Auwers, and others who in the past have considered the relation of refraction to chemical composition. More recent data have been assembled by Egloff (1946) and the American Petroleum Institute (1953); Timmermans (1950), after "systematic recourse to the whole of the chemical literature up to January 1st, 1950" cites those physico-chemical constants which he judges to have been "established with a precision worthy of contemporary science"; Vogel, in papers to the *J. Chem. Soc.* during the last thirty years, has provided new measurements of the refractive index of nearly 900 compounds. Many others, of varying accuracies, can be traced through the "Tables of Experimental Dipole Moments" lately prepared by McClellan (1963).

The refractive index of a substance varies with the physical state of the latter, the temperature t, and the wave-length λ of the light by which n is observed. The first two of these effects were early attributed to the density d. In 1805 Laplace, arguing from Newton's corpuscular theory of light, deduced that $(n^2-1)/d$ should be constant, but subsequent experiments by Arago and Petit showed this quotient for a liquid and its vapour to be not the same. Empirically, Gladstone and Dale (1858) found that $(n-1)/d$ was adequately independent of temperature throughout a given state, and they and other workers proceeded to analyse $(n-1)/d$ as an "additive-constitutive" property; Smiles (1910) gives a full account of this phase. However, the Gladstone-Dale expression imperfectly covered changes of state. More satisfactory in several respects was the equation (1), published almost simultaneously by Lorenz (of Copenhagen) and Lorentz (of Leyden) during 1880:

$$(n^2-1)/(n^2+2)\,d = \text{constant} = r \tag{1}$$

Lorenz derived (1) by assuming that a material is made up of spherical molecules through which light travels slower than in the vacuum in which they are situated, while Lorentz proceeded logically from Maxwell's electromagnetic theory and was thus able to explain, in addition, the variations of n with λ (dispersion). In fact, however, exact compensation of n by d is not achieved by the left-hand side of (1), which with liquids may increase numerically by about 0·01% per degree of temperature rise; greatest invariance is represented by the expression of Eykman (1895):

$$(n^2-1)/(n+0{\cdot}4)\,d = \text{constant} \tag{2}$$

Although empirical and lacking a theoretical basis, (2) is useful for interpolation purposes. Lorentz (1909) himself pointed out possible causes for the slight limitations of (1), and Böttcher (1952) has discussed an appropriate correction; nevertheless, in practice the inconstancy of (1) with temperature is usually within the experimental error and the equation may safely be used as written above.

II. MOLECULAR REFRACTION

The specific refraction r of a substance multiplied by the molecular weight is the molecular refraction: $Mr = R$; with d in g/cm^3, R is in cm^3 units. R, of course, is affected by the dispersion of n, so the wavelength should be specified (e.g. for carbon tetrachloride, $R_{\mathrm{C}} = 26{\cdot}31$, $R_{\mathrm{D}} = 26{\cdot}45$, $R_{\mathrm{F}} = 26{\cdot}86$, $R_{\mathrm{G'}} = 27{\cdot}08$ cm^3; the four wavelengths indicated are those which have most frequently been used in the past: $\mathrm{C} = \mathrm{H}_\alpha = 6563$ Å, $\mathrm{D} = \mathrm{Na} = 5893$ Å, $\mathrm{F} = \mathrm{H}_\beta = 4861$ Å, $\mathrm{G'} = \mathrm{H}_\gamma = 4341$ Å).

With liquids, the requisite n_λ and d_4^t measurements can obviously be made directly; solids, in general, are examined in solution, and "mixture formulae" applied to the observations. If subscripts 1, 2, and 12 relate respectively to solvent, solute, and solution, and if concentrations are expressed as molar fractions f_1 and f_2, or weight fractions w_1 and w_2, the apparent partial molar or specific refractions (R_2 or r_2) can be extracted from equations (3) or (4), provided R_1 or r_1 is invariant with concentration:

$$(n_{12}^2-1)(M_1f_1+M_2f_2)/(n_{12}^2+2)\,d_{12} = R_1f_1+R_2f_2 \tag{3}$$

$$(n_{12}^2-1)/(n_{12}^2+2)\,d_{12} = w_1r_1+w_2r_2 \tag{4}$$

Weight fractions are arithmetically simpler in use than molar fractions. Since it is often found by experiment that $(d_{12}-d_1)/d_1w_2 = \beta$ and $(n_{12}^2-n_1^2)/w_2 = \gamma n_1^2$ are constant, r_2 at infinite dilution can be easily obtained from mean values of β and γn_1^2 by (5):

$$_\infty r_2 = r_1(1-\beta)+C\gamma n_1^2 \tag{5}$$

where $C = 3/d_1(n_1^2+2)^2$; cf. Le Fèvre (1953).

Crystalline solids frequently exhibit anisotropy in their refractive indices, uniaxial crystals having two, n_ϵ and n_w, and biaxial crystals having three, n_α, n_β, and n_γ, characteristic refractive indexes, in such cases the geometric mean is usually taken as $\bar{n}$ for insertion in (1): $\bar{n} = (n_\epsilon^2 n_w)^{1/3}$ or $\bar{n} = (n_\alpha n_\beta n_\gamma)^{1/3}$ (cf. Heigl and Wulff, 1931, for examples).

A. "*Additivity*" *of Molecular Refraction*

The efforts of early workers, from Herschel in 1830, through Berthelot, Gladstone and Dale, Landolt, to Conrady, Brühl and others in the 1890's (cf. Smiles, 1910, for references) demonstrated the existence of connections between refraction and chemical composition. In particular, Berthelot, using the product of $(n^2-1)/d$ and the equivalent weight, found equal differences for equal differences of CH_2 in analogous compounds, while Gladstone and Dale (1863), explicitly concluded that $(n-1)/d$ for a given liquid was made up from corresponding values for the component elements "modified by the manner of combination". Brühl (1880) adopted $M(n^2-1)/d(n^2+2)$ and, surveying about 150 substances, carried through the first extensive analysis of R from the viewpoint of additivity, and compiled a list of "atom refractions". These last were easily obtained once the constant difference for CH_2 was established by measurements of molecular refractions for a number of homologous series; then e.g. subtraction of xR_{CH_2} from the refraction of a hydrocarbon C_xH_{2x+2} gave $2R_{hydrogen}$, of $(xR_{CH_2}+R_{hydrogen})$ from the refraction of $C_xH_{2x+1}.X$, gave $R_{atom\,X}$, of $2R_{hydrogen}$ from R_{CH_2} gave R_{carbon}, etc. Brühl noted the "constitutivity" of this property: the atom refractions of oxygens were not the same in aldehydes, acids, and ethers; R_{carbon} varied dependently on the carbon being singly, doubly, or triply bonded (and by comparing the R's of related saturated and unsaturated molecules, knowing $R_{hydrogen}$, he evaluated the increments in refractivity due to multiple linkages between carbon and carbon); later (1886a, b) he drew attention to the effects of conjugated unsaturation, and reported the range of atom refractions necessary for nitrogen in several classes of its compounds (1895, 1897, 1898). To illustrate these points some of Brühl's refractivities are given in Table 1.

By starting from such values, and reversing the arguments through which they were obtained, a way of solving problems of molecular constitution was opened. As the approach involved no destruction of materials or disturbance of equilibria, molecular refractions quickly became extensively applied to a variety of structural questions, particularly to those difficultly resolved by the ordinary chemical techniques of the time, e.g. the positions of double bonds in terpenes, the recognition of

TABLE 1

Some Refractivities[a] Deduced by Brühl

C	2·365	O (in carbonyl group)	2·328
H	1·103	O (in ethers)	1·655
Cl	6·014	O (in hydroxyl group)	1·506
Br	8·863	Ethylene bond	1·836
I	13·808	Acetylene bond	2·22
N (in AlkylNH_2)	2·31	N (in ArylNH_2)	3·01
N (in $Alkyl_2NH$)	2·60	N (in $Aryl_2NH$)	3·40
N (in $Alkyl_3N$)	2·92	N (in $Aryl_3N$)	4·10

[a] For the H_α line

geometrical isomers, the examination of keto-enol systems, etc. Brühl died in 1911. A Royal Institution "Friday Evening Discourse" (Brühl, 1906) made available to British chemists an account (in English) of his optical-chemical researches. (According to an anonymous writer (1911), Brühl gave this lecture in a "masterly manner" which obviously considerably impressed the audience.) A long obituary by von Auwers (1911) contains more details, both scientific and personal, and includes a complete list of references to Brühl's publications. Brühl can justly be credited with having pioneered one of the first generally useful methods of physical-organic chemistry.

His constants were revised and extended by von Auwers and Eisenlohr from 1910 onward; Table 2 is an extract from Eisenlohr's 1923 data. Although the amendments to Brühl's figures appear slight it is important to remember that the R_λ's shown are mean values.

As measurements accumulated, the constitutive nature of this property became more and more obvious. Even the "constant" for the methylene group depended somewhat upon the homologous series from which it was drawn. Concealed beneath the average R_α of 4·59 cm^3, quoted by Eisenlohr (1910), after recalculating Brühl's values, were the facts that although 66 hydrocarbons, 92 aldehydes and ketones, 74 acids, 81 alcohols, and 190 esters, gave average R_α's of 4·60, 4·60, 4·59, 4·61, and 4·58 respectively, individual fluctuations within a series were sometimes between 4·11 and 4·86 cm^3 (Vahrman's 1960 estimate of 4·63 cm^3 falls within this range). Increments appropriate to double and triple bonds seemed to vary with the number and length of the radicals attached, Eykman (1906) suggesting 1·51, 1·60, 1·75, 1·88, and *ca.* 2·00 cm^3 as $CH_2{=}CH_2$ by progressive substitution became $CR_2{:}CR_2$. Von Auwers (1935) proposed 2·325 cm^3 for $C{\equiv}C$ when terminally situated or 2·573 cm^3 when within a chain, and Campbell and Eveslage

TABLE 2

Some Refractivities Deduced by Eisenlohr

	R_α	R_D	R_β	R_γ
C	2·413	2·418	2·438	2·466
H	1·092	1·100	1·115	1·122
Cl	5·933	5·967	6·043	6·101
Br	8·803	8·865	8·999	9·152
I	13·757	13·900	14·224	14·521
O (in carbonyl group)	2·189	2·211	2·247	2·267
O (in ethers)	1·639	1·643	1·649	1·662
O (in hydroxyl group)	1·522	1·525	1·531	1·541
Ethylene bond	1·686	1·733	1·824	1·893
Acetylene bond	2·328	2·398	2·056	2·538
N (in AlkylNH_2)	2·309	2·322	2·368	2·397
N (in Alkyl_2NH)	2·478	2·502	2·561	2·605
N (in Alkyl_3N)	2·808	2·840	2·940	3·000

(1945) gave higher values still for internal bonds (2·267, 2·534, 2·696, 2·735, and 2·767 cm^3, in order, for 1-, 2-, 3-, 4-, and 5-acetylenes). According to Huggins (1941) the molecular refractions of saturated hydrocarbons are not strictly additive functions of atomic refractivities but are influenced by the types and amounts of chain-branching within their molecules. The variability of nitrogen and oxygen in their different combinations has already been mentioned. The analogous behaviour of sulphur (exhibiting atom refractions, for the H$_\alpha$ line, from 3·34 in diethyl sulphate to 9·31 cm^3 in diphenyl sulphide) and of other multivalent elements, has long been known (cf. Smiles, 1910, p. 277).

Inevitably, in view of the apparent imperfections, "additive" treatments of molecular refraction have been criticized. Brühl has been accused of inconsistency in allotting increments for double or triple bonds between carbon and carbon but not for those between carbon and oxygen or carbon and nitrogen . . . "one might just as well use only one atomic constant for oxygen, add an increment for C=O, and use different atomic constants of hydrogen depending on whether it is bonded to carbon or oxygen. A corresponding remark applies to the distinction between the three atomic constants of nitrogen in primary, secondary, and tertiary amines. In the first two, some of the hydrogen atoms are bonded to carbon and some to nitrogen, and it is arbitrary to ascribe the optical differences only to the nitrogen" (Fajans, 1949 *a*, *b*).

Notwithstanding these and other objections the fact remains that tables such as Table 2 have an empirical usefulness for the testing of, or deciding between, the various formulae often available for a given compound. Minor imperfections in additivity can be diminished if—as Eykman (1893) originally suggested—refractive values for groups are chosen from the measured molecular refractions of the nearest complete molecules (e.g. R for phenyl from R found for benzene minus R_H); major departures from additivity can offer significant evidence on questions of structure or configuration. Two important illustrations are provided by poly-unsaturated and geometrically isomeric molecules.

Brühl (1886a) had noted that the effect of unsaturation on molecular refraction could not always be represented by the increments previously deduced: two olefinic bonds when situated conjugatively increased the refraction abnormally, the difference between observed and calculated R's being regarded as "optical anomaly". In 1907 he introduced the terms "optical exaltation" and "optical depression" to refer respectively to cases where the observed R exceeded or fell short of that calculated; numerically, depressions are commonly small but exaltations may be very large (see Smiles, 1910; von Auwers, 1924):

	R_α *observed*	R_α *calc.*	ΔR cm^3
Benzene	25·93	26·31	−0·38
Diphenylmethane	55·13	55·00	+0·13
Styrene	35·98	35·08	+0·90
Phenylacetylene	34·46	33·53	+0·93
Bibenzyl	59·60	59·64	−0·04
Stilbene	65·65	59·20	+6·45
1,4-Diphenylbutadiene	82·9	68·0	+14·9
Diphenyldiacetylene	74·86	64·86	+10·0
1,6-Diphenylhexatriene	100·9	76·74	+24·2
Mesityl oxide	30·13	29·39	+0·74
Phorone	45·39	42·73	+2·66
Benzaldehyde	31·77	31·01	+0·76
Cinnamaldehyde	43·51	39·78	+3·73
Carvenone	46·92	45·81	+1·11

The occurrence of positive exaltation has been frequently cited when fixing the relative positions of C=C and C=O units in structures containing two or more of these bonds; many examples are to be found in terpene chemistry (cf. Semmler, 1906; Gildemeister and Hoffman, 1928–31; or Simonsen, 1947–9).

Brühl (1896) stated that, as a general rule, among geometrical isomerides the more stable, higher melting, and less soluble individual had the greater molecular refraction; when the groups attached to the double bond were unsaturated the disparity between R_{trans} and R_{cis} was numerically more marked:

	R_α cm^3
Oleic acid	86·50
Elaidic acid	86·67
Ethyl maleate	42·23
Ethyl fumarate	42·90
Anisaldoxime (syn)	44·85
Anisaldoxime (anti)	45·03

Such defective additivity has proved useful for structural assignments between isomers; notably it has been invoked during the reconsideration of the natures of the aromatic diazo- and azo-compounds (see summary by Calderbank *et al.*, 1948). Departures from additivity due to ring formation have also been utilized in structural investigations (e.g. Semmler (1906) used refraction to confirm the presence of 3-membered rings in sabinene and tanacetone) but here caution is necessary because exaltations are not uniformly associated with ring-size, seemingly being different in homo- and hetero-cyclic systems (cf. Hughes and Johnson, 1931).

It is clear therefore that the empirical value of data such as Brühl and Eisenlohr attempted to provide depends very much on the range and details of the molecular environments from which the atomic and structural constants have been drawn.

During the last three decades a most comprehensive overhaul and extension of previous sources has been undertaken by Vogel (refs. from 1934 onward; see also refs. to Vogel under Cowan, Cresswell, Grzeskowiak, Jeffery, and Kyte). By 1948 the individual molecular refractions for the C, D, F, and G′ spectral lines had been recorded for 606 compounds whose purity criteria were also given; from this information Vogel deduced the values reproduced in Table 3. In addition, throughout his work Vogel has regularly listed for each substance the magnitude of the product Mn_D^{20}—the so-called "molecular refraction coefficient" (Eisenlohr, 1925)—which, although devoid of foundation in theory, can in practice be split into additive-constitutive atomic and group coefficients. These last have been included in Table 3 since they make possible the prediction of n_D^{20} for a liquid from its corresponding structural formula and molecular weight.

Alternative analyses of refractometric data have been proposed, e.g. using G. N. Lewis' (1923) ideas of valence and electronic bonding, Fajans and Knorr (1924) and independently Smyth (1925) deduced refractivities for octets and electron groups; von Steiger (1921), Denbigh

TABLE 3

Atomic, Group, and Structural Refractivities given by Vogel[a]

	R_C	R_D	R_F	$R_{G'}$	Mn_D^{20}
H (in CH_2)	1·026	1·028	1·043	1·040	−2·56
C (in CH_2)	2·572	2·591	2·601	2·655	25·71
O (in ethers)	1·753	1·764	1·786	1·805	22·74
O (in acetals)	1·603	1·607	1·618	1·627	22·41
CO (in ketones)	4·579	4·601	4·654	4·702	42·41
CO (in methyl ketones)	4·730	4·758	4·814	4·874	42·42
COO (in esters)	6·173	6·200	6·261	6·315	64·14
OH (in alcohols)	2·536	2·546	2·570	2·588	23·94
CO_2H	7·191	7·226	7·308	7·368	63·98
F	0·81	0·81	0·79	0·78	21·84
Cl	5·821	5·844	5·918	5·973	50·41
Br	8·681	8·741	8·892	9·011	118·07
I	13·825	13·954	14·310	14·620	196·27
NH_2 (1^{ary} aliph. amines)	4·414	4·438	4·507	4·570	22·64
NH (2^{ary} aliph. amines)	3·572	3·610	3·667	3·732	23·34
NH (2^{ary} arom. amines)	4·548	4·678	5·000	5·273	29·52
N (3^{ary} aliph. amines)	2·698	2·744	2·820	2·914	24·37
N (3^{ary} arom. amines)	4·085	4·243	4·675	5·155	30·23
NO (nitroso)	5·130	5·200	5·397	5·577	43·14
O.NO (nitrite)	7·187	7·237	7·377	7·507	62·27
NO_2 (nitro)	6·662	6·713	6·823	6·928	65·61
N.NO (nitrosamine)	7·748	7·850	8·100	8·358	69·67
S (in sulphides)	7·852	7·921	8·081	8·233	52·86
SH (in thiols)	8·691	8·757	8·919	9·057	50·20
CS (in xanthates)	12·84	13·07	13·67	14·22	77·20
SCN (in thiocyanates)	13·313	13·400	13·603	13·808	88·90
NCS (in isothiocyanates)	15·445	15·615	15·980	16·300	93·11
CN (in nitriles)	5·431	5·459	5·513	5·561	36·46
C:C increment[b]	1·545	1·575	1·672	1·720	−6·07
C≡C increment[b]	1·959	1·977	2·061	2·084	−12·56
3-carbon ring[c]	0·592	0·614	0·656	0·646	−4·72
4-carbon ring[c]	0·303	0·317	0·332	0·322	−4·67
5-carbon ring[c]	−0·19	−0·19	−0·19	−0·22	−4·56
6-carbon ring[c]	−0·15	−0·15	−0·16	−0·17	−3·53
CH_2	4·624	4·647	4·695	4·735	20·59
CH_3	5·636	5·653	5·719	5·746	18·13
C_2H_5	10·260	10·300	10·414	10·481	38·72
n-C_3H_7	14·895	14·965	15·125	15·235	59·25
iso-C_3H_7	14·905	14·975	15·145	15·255	58·95
n-C_4H_9	19·500	19·585	19·800	19·950	79·81
iso-C_4H_9	19·530	19·620	19·840	19·990	79·54
s-C_4H_9	19·330	19·420	19·625	19·775	80·21
n-C_5H_{11}	24·140	24·250	24·515	24·700	100·46
n-C_6H_{13}	28·725	28·855	29·160	29·385	121·10
n-C_7H_{15}	33·395	33·550	33·905	34·170	141·75
n-C_8H_{17}	37·960	38·135	38·535	38·830	162·43
C_3H_5 (allyl)	14·425	14·520	14·745	14·920	57·60
C_6H_5 (phenyl)	25·136	25·359	25·906	26·356	122·03

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[a] *J. chem. Soc.* 1948, p. 1842. [b] Terminal bonds. [c] Increments.

(1940), and more recently Vogel (Cresswell *et al.*, 1952) have developed a system of "bond refractions". Smyth and von Steiger started from atomic refractions, such as are in Table 3, and argued that a quarter of the refractivity of carbon is contributed to a single bond, two quarters to a double bond, etc., so that $R_{\text{C—H}} = 0{\cdot}25R_{\text{carbon}} + R_{\text{hydrogen}}$, $R_{\text{C—C}} = 0{\cdot}5R_{\text{carbon}}$, $R_{\text{C=C}} = R_{\text{carbon}} + R_{\text{double bond}}$, $R_{\text{C}\equiv\text{C}} = 1{\cdot}5R_{\text{carbon}} + R_{\text{triple bond}}$, $R_{\text{C=O}} = 0{\cdot}5R_{\text{carbon}} + R_{\text{ketonic oxygen}}$, and so on. The imperfect additivity of the earlier atomic and structural refractivities is, of course, carried over to bond refractivities by such derivations. The bond refractions of Denbigh or Vogel depend directly upon molecular refractions determined by experiment: fundamentally the value found for the methylene group in a homologous series can be written as $R_{\text{CH}_2} = R_{\text{C—C}} + 2R_{\text{C—H}}$ and, correspondingly, the molecular refraction for any n-alkane is

$$(n-1)R_{\text{C—C}} + (2n+2)\,R_{\text{C—H}} = R_{\text{C}_n\text{H}_{2n+2}}$$

the left-hand side of which, with $a = R_{\text{C—C}} + 6R_{\text{C—H}}$ and $b = R_{\text{C—C}} + 2R_{\text{C—H}}$, becomes $a + b(n-2)$.

Denbigh and Vickery (1949) used the Na—D light refractions of eight n-alkanes, containing five or more carbon atoms, with which to compute (by the method of least squares) the "best fit" rectilinear relation between R_{alkane} and $(n-2)$. In this way, the constants emerged as $a = 11{\cdot}339$ and $b = 4{\cdot}644$, whence $R_{\text{C—H}} = 1{\cdot}674$ and $R_{\text{C—C}} = 1{\cdot}296\ \text{cm}^3$. These results were then tested on 43 n-alkanes and 153 branched alkanes. Calculated and measured molecular refractions showed an average discrepancy over the whole range of 0·43%. The positive discrepancies, averaging 0·37%, occurred predominantly among the higher n-alkanes, the negative discrepancies, averaging 0·46%, lay almost wholly among the branched alkanes. Statistically these divergencies were not attributable to random errors. Accordingly Denbigh and Vickery suggested small corrective "increments" for four types of branching: a methyl group in the 2-position carrying an exaltation of $0{\cdot}026 \pm 0{\cdot}011\ \text{cm}^3$ in contrast to one within the chain causing a depression of $0{\cdot}143 \pm 0{\cdot}016\ \text{cm}^3$, and depressions of $0{\cdot}244 \pm 0{\cdot}026$ and $0{\cdot}307 \pm 0{\cdot}030\ \text{cm}^3$ being required for ethyl and "larger substituents" respectively. As often noted with physical properties of first members of homologous series, the R_{D} of methane ($6{\cdot}588\ \text{cm}^3$) may be slightly anomalous—it yields an estimate for $R_{\text{C—H}}$ ($1{\cdot}647\ \text{cm}^3$) which is smaller than that deduced ($1{\cdot}674\ \text{cm}^3$) from pentane and higher hydrocarbons.

The "smoothing" procedure of Denbigh and Vickery diverts attention from a feature which occurs irregularly among different families of compounds: the refractivities of CH_2 groups (i.e. the values of b above) sometimes alternate as methylenes are inserted to extend the lengths of