NOTES

The Relation between Magneto-optic Rotation and Refractive Dispersion of Hydrocarbons

By A. Bondi

Inspection of data on the magneto-optic rotation (Verdet Constant, V) of hydrocarbons[1,2] suggested that they may be directly proportional to the refractive dispersion, $n_{\nu 1} - n_{\nu 2} = \Delta n$. The recent extensive and accurate data published by Foehr[3] make possible the quantitative comparison which is presented in Table I. It appears that $V/\Delta n$ is indeed very nearly independent of the hydrocarbon type at low molecular weights and substantially constant in the higher molecular weight range.

The greatest "exaltation" apparently occurs among the aromatic hydrocarbons, but too few measurements are available in this class of compounds to permit any valid generalization.

As a practical result this observation suggests that refractive dispersion and magneto-optic rotation may be used interchangeably. Since refractive dispersion data are usually more accessible[4,5] than Verdet constants, the ingenious scheme of (magneto-optic) hydrocarbon type analysis proposed by Foehr[3] may now be applied more extensively.

The theoretical background is contained in the Becquerel formula[6]

$$V = \gamma \frac{e}{2mc^2} \nu \frac{\partial n}{\partial \nu} \tag{1}$$

where the universal factor $e/2\text{mc.}^2$ derives from the Larmor precession, ν = frequency of the light used, $\partial n/\partial \nu$ = refractive dispersion, γ = "anomaly" factor. The constancy of the ratio $V/\Delta n$ thus means that for hydrocarbons γ is a constant. For diamagnetic substances, according to Schütz[6]

$$\gamma = a_i + \frac{b}{2} \frac{\nu_i}{\Delta \nu_0} \qquad \text{if } \nu \ll \nu_i \tag{2}$$

where a_i = oscillator strength, ν_i = characteristic frequency of the electron transition which is active in the magneto-rotation and determines the dispersion of V (as well as of the refractivity, v. i.), $\Delta \nu_0$ = multiplet splitting shift, and b = a numerical factor of the order $-{}^2/_3$.[6] No data are yet available on the multiplet splitting term, $\Delta \nu_0$, of organic molecules, but it is likely to be equal for all hydrocarbons. Equation (2) therefore implies the existence of a linear relation between the oscillator strength and the characteristic frequency of the "dispersion-electron" of hydrocarbons.

As one can observe the constancy of γ within other families of organic molecules,[6] this relation should hold more widely. The lack of reliable absolute intensity data, particularly in the vacuum ultraviolet where the characteristic absorption band of the saturated hydrocarbons is located, precludes a direct test of the postulate made. The constancy of γ in spite of the wide variation in ν_i (0.8 to 2.5×10^{15} sec.$^{-1}$) and in a_i encountered in the range of hydrocarbons reported in Table I suggests, however, that a relationship at least similar to the proposed one exists. (A plot of the oscillator strength f_1,[7] *versus* ν_1 shows that the data lie on smoothly ascending curves, which are, however, characteristic of each family of (aromatic) hydrocarbons so tested, and not universal for all hydrocarbons as first hoped for.) The utility of Equation (2) for γ = const. consists in the possibility of expressing the refractive dispersion of hydrocarbons as a function of ν_i alone, thereby facilitating the rational treatment of this easily determined physical property.

TABLE I

COMPARISON OF VERDET CONSTANT[a] AND REFRACTIVE DISPERSION[b] OF HYDROCARBONS

Substance	$V_D \times 10^2$	$V/\Delta n$[c]	$\Delta V/\Delta n$[d]
n-Pentane	1.159	1.188	1.11
n-Decane	1.316	1.148	1.05
n-Hexadecane	1.359	1.12	1.03
11-*n*-Decyldocosane	1.423	1.12	1.01
Cyclopentane	1.238	1.08	0.96
Cyclohexane	1.247	1.05	.93
11-Cyclohexyl-*n*-heneicosane	1.440	1.12	1.00
1.1-Dicyclohexyl-*n*-heptane	1.443	1.11	0.99
Benzene	3.02	1.11	1.09
Toluene	2.726	1.065	1.11
Ethylbenzene	2.60	1.05	..
n-Propylbenzene	2.46	1.015[e]	..
p-Methylisopropylbenzene	2.30	0.986[e]	..
Diphenylmethane	3.38	1.04	..
Naphthalene	5.33	1.11	..
Methylnaphthalene	4.48	0.94[e]	1.105
Average	..	1.08 av. deviation ±0.05	..

[a] From Ref. 3. [b] From Ref. 4 and 5. [c] $\Delta n = n_{G'} - n_c$. [d] $V = V_{4359} - V_D$. [e] These scattered values may be due to inaccurate refractive dispersion data.

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(1) M. Scherer, "Pub. sci. tech. ministere de l'air," France, No. 50, (1934), p. 1-91. "Science of Petroleum," Vol. 2, London, 1938, p. 1220.

(2) S. Broersma, H. I. Waterman, J. B. Westerdijk and E. C. Wiersma, *Physica*, **10**, 97 (1943).

(3) E. G. Foehr, Ph.D. Thesis, Pennsylvania State College, 1944.

(4) R. E. Thorpe and R. G. Larsen, *Ind. Eng. Chem.*, **34**, 853 1942).

(5) W. J. C. de Kok and H. I. Waterman, *Chem. Weekblad*, **37**, 454 (1940).

(6) W. Schütz, "Magnetooptik" in Wien-Harms Handb. der Experimental physik, Vol. 16, Part 1, Leipzig, 1936, p. 80-141.

(7) From unpublished experimental data by Spectroscopic Department, Shell Development Co., Emeryville, Calif.

Since the dispersion of both the refractivity and the Verdet constant is governed by the term $\Sigma A_i/(\nu_i^2 - \nu^2)$, constancy of the ratio $\Delta V/\Delta n$ would be indicative of the fact that the electronic transitions responsible for both are identical. The data in the last column show that this expectation is essentially fulfilled, as has also been found for various aliphatic oxygen compounds.[8]

[8] W. J. Lewis and E. J. Evans, *Phil. Mag.*, **13**, 265 (1932).

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The Cryoscopic Behavior of 1,1-Dimethylcyclohexane Containing Certain Hydrocarbon Impurities[1]

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A short investigation has been made concerning the cryoscopic behavior of 1,1-dimethylcyclohexane upon introduction of certain selected hydrocarbon impurities. This study was prompted by the observation that introduction of a small amount of *cis*-1,2-dimethylcyclohexane as an impurity in 1,1-dimethylcyclohexane caused an increase in the freezing point of the latter hydrocarbon, instead of the normal lowering. Although similar irregularities caused by solid solution formation have been observed in several binary hydrocarbon systems studied in detail by other workers,[3,4,5,6] it was thought that this new information would prove helpful because of the widespread reliance on cryoscopic data as criteria of purity.

The results of this investigation are summarized in Table I.

It will be noted that of the solutes used only *n*-heptane and *n*-butylcyclohexane produced normal freezing point lowering; *cis*-1,2-dimethylcyclohexane actually raised the freezing point, and the remaining solutes caused only a fraction of the normal lowering. In every case of abnormal behavior the apparent purity as calculated from the freezing point data was, of course, too high.

TABLE I

CRYOSCOPIC BEHAVIOR OF 1,1-DIMETHYLCYCLOHEXANE CONTAINING HYDROCARBON IMPURITIES

Solute (impurity)	Total mole % impurity added	Freezing point (°C.)	Observed Δt (°C.)	Expected[a] Δt (°C.)	Actual purity[b] (mole %)	Apparent purity[a] (mole %)
None added	0	−35.83 ± 0.04	....	....	99.04	...
cis-1,2-Dimethylcyclohexane	0.931	−35.66 ± .05	+0.17	−2.25	98.11	99.11
	1.97	−35.42 ± .07	+0.41	−4.79	97.07	99.21
None added	0	−35.52 ± .04	....	....	99.17	...
trans-1,2-Dimethylcyclohexane	0.648	−35.58 ± .04	−0.06	−1.57	98.52	99.15
	1.33	−35.69 ± .06	−0.17	−3.22	97.84	99.10
None added	0	−36.21 ± .03	....	....	98.88	...
trans-1,4-Dimethylcyclohexane	0.676	−37.23 ± .02	−1.02	−1.66	98.20	98.4[illegible]
	1.35	−38.39 ± .05	−2.18	−3.29	97.53	97.98
None added	0	−35.64 ± .02	....	....	99.12	...
Cyclohexane	1.26	−36.44 ± .04	−0.80	−3.05	97.86	98.79
	2.30	−37.09 ± .03	−1.45	−5.59	96.82	98.52
None added	0	−35.79 ± .03	....	....	99.06	...
2,2,3-Trimethylbutane	0.671	−35.97 ± .03	−0.18	−1.62	98.39	98.98
	1.59	−36.10 ± .05	−0.31	−3.85	97.47	98.93
None added	0	−35.58 ± .04	....	....	99.15	...
n-Heptane	0.798	−37.49 ± .02	−1.91	−1.92	98.35	98.36
	1.19	−38.36 ± .02	−2.78	−2.87	97.96	98.00
None added	0	−35.74 ± .05	....	....	99.08	...
n-Butylcyclohexane	0.643	−37.25 ± .05	−1.51	−1.54	98.44	98.45
	1.04	−38.23 ± .04	−2.49	−2.52	98.04	98.05

[a] These data were calculated from the approximate equation $\log_{10} p = 2 - (A/2.303)(t_{f_0} - t_f)$ where p = purity (actual or apparent) in mole per cent., t_{f_0} = freezing point at 100% purity t_f = experimental freezing point (actual or expected) and $A = \Delta H^\circ_m/RT_{f_0}$ in which ΔH°_m is the heat of fusion (per mole). Values for t_{f_0} (−33.54°) and A (0.0042 deg.$^{-1}$) had been given by the American Petroleum Institute Research Project 44 in Selected Values of Properties of Hydrocarbons (Circular of the National Bureau of Standards C461) Table 7z. [b] The original purity of each sample was calculated from its freezing point using the equation and data mentioned in footnote *a*, assuming that no impurity leading to abnormal behavior was already present. The subsequent (lower) purities were obtained from the original purities by subtracting the mole percentages of impurity added.

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[3] Smittenberg, Hoog and Henkes, THIS JOURNAL, **60**, 17 (1938).

[4] Took and Aston, *ibid.*, **67**, 2275 (1945).

[5] Fink, Cines, Frey and Aston, *ibid.*, **69**, 1501 (1947).

[6] Hirschler, King and Faulconer, paper presented before the Petroleum Division at the Chicago, Illinois, meeting of the American Chemical Society, April, 1948.