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# The Extension of Bond and Molar Refraction Concepts to Liquid Organic Phosphorus Compounds

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By combining the Denbigh bond refraction concept with Eisenlohr's "molecular refraction coefficient," a simple and useful relation has been established between refractive index and molecular structure of liquid organic phosphorus compounds.

In the field of phosphorus compounds, correlation of refractive index and structure first was attempted by Zecchini,[1] who determined the molar refractivities[2] of five inorganic and six organic phosphorus compounds. From each of the eleven molar refractivities, he calculated the atomic refractivity of phosphorus, obtaining values ranging from 2.81 to 11.79. Almost equally discordant values were reported by Jones, Davies and Dyke,[3] whose work was based on about 60 phosphorus compounds (mostly organic), and whose values for the atomic refractivity of phosphorus ranged from 4.36 in certain esters to 10.40 in certain substituted phosphines. Recent investigators[4] have adopted at least seven special values, ranging from 3.75 to 8.44, for the atomic refractivity of phosphorus in various types of esters. For dithiophosphoric acid esters and related compounds, Kabachnik and Mastryukova[5] retained a constant value 9.14 for phosphorus but used varying values for sulfur.

The foregoing makes abundantly clear the need for a new approach in order to bring the refractive index of a phosphorus compound into satisfactory relation with its structure. For some time, the requisite basis for such an approach has been at hand in the work of Vogel,[6] who has utilized two concepts which appear to have been entirely overlooked by chemists working in the field of phosphorus compounds. The first of these concepts stems from the classical monograph of Eisenlohr,[7a] wherein brief mention was made of some previously unpublished work on an empirical expression called "molecular refraction coefficient"; since this is merely the arithmetical product of the molecular weight and the refractive index $n^{20}_{\mathrm{D}}$ and is in no sense a coefficient, the more rational name "molar refraction product," symbolized as $Mn^{20}_{\mathrm{D}}$ or as $MR_{\mathrm{E}}$, seems preferable. Although Eisenlohr published several subsequent articles[7b] on the subject, Vogel seems to have been the only other chemist who perceived the usefulness of the relation. From his own measurements on a large number of organic compounds, he constructed a table[6a] showing 56 atomic refractivities (based on the Lorenz–Lorentz equation), together with 56 corresponding numbers represented merely by the symbol $Mn^{20}_{\mathrm{D}}$. Inasmuch as these are numbers from which approximations to Eisenlohr's molar refraction products may be obtained by mere addition, they may appropriately be called "atomic refraction constants."

The second notable advance was made when Vogel adopted the bond refraction concept of Denbigh,[8] according to which the phenomenon of refraction is attributable to the bonding electrons between atoms rather than to the atoms themselves. The system devised by Denbigh was of course based on the Lorenz–Lorentz expression; it has been used with marked success by Warrick[9] in the field of organosilicon compounds, by West and Rochow[10] in that of organotin compounds, and more recently by Vogel[6c] for a variety of organometallic compounds. All of these authors have followed Denbigh's example in using the term "bond refractions" for numbers which they derived from the Lorenz–Lorentz equation; in the Partington terminology here employed, they are called "bond refractivities." Vogel translated all of his previous data into a tabulation[6b] of 34 of these values together with the corresponding 34 numbers to which he gave the name "bond refraction coefficients," but which, having been derived from Eisenlohr molar refraction products, are more appropriately called "bond refraction constants." Apart from the tabulation proper, which contained no values relating to phosphorus, it should be noted that Vogel[6d] made preliminary estimates ranging from 3.00 to 3.22 for the bond refractivity of P–O and from −1.13 to −1.51 for that of P=O.

The object of the present work is to show the

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[1] F. Zecchini, *Gazz. chim. ital.*, **23**, 97 (1893); **24**, 34 (1894).

[2] The quantity defined by the Lorenz–Lorentz equation $\left(MR_{\mathrm{L}} = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}\right)$ is currently called "molar refractivity" by some authors and "molar refraction" by others. In accordance with the terminology of Partington in Vol. IV of his "Advanced Treatise on Physical Chemistry," the former name will be used in the present work, as well as the terms "atomic refractivity" and "bond refractivity" for derived quantities which add up approximately to molar refractivity. A somewhat analogous terminology, suggested by Dr. J. H. Fletcher of these laboratories, will be employed for correlation systems based on the empirical Eisenlohr relation referred to in the text.

[3] W. C. Jones, W. J. Davies and W. J. C. Dyke, *J. Phys. Chem.*, **37**, 583 (1933).

[4] (a) M. I. Kabachnik, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 219 (1948); *C. A.*, **42**, 5736 (1948); (b) G. M. Kosolapoff, THIS JOURNAL, **73**, 4989 (1951); (c) M. I. Kabachnik and E. S. Shepeleva, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 862 (1953); *C. A.*, **49**, 843 (1955); (d) A. Razumov and O. Mukhacheva, *Zhur. Obshchei Khim.*, **26**, 1436 (1956); *C. A.*, **50**, 14325 (1956).

[5] (a) M. I. Kabachnik and T. A. Mastryukova, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 727 (1952); *C. A.*, **47**, 9909 (1953); (b) 436 (1954); *C. A.*, **49**, 9559 (1955).

[6] (a) A. I. Vogel, *J. Chem. Soc.*, 1842 (1948); (b) A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *ibid.*, 531 (1952); (c) A. I. Vogel, W. T. Cresswell and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954); (d) A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, *J. Chem. Soc.*, 535 (1952); (e) A. I. Vogel and D. M. Cowan, *ibid.*, 24 (1943).

[7] (a) F. Eisenlohr, "Spektrochemie Organischen Verbindungen," Enke, Stuttgart, 1912, pp. 12–14; (b) F. Eisenlohr and E. Wöhlisch, *Ber.*, **53**, 1746 (1920); F. Eisenlohr, *ibid.*, **53**, 2053 (1920); **54**, 299 (1921); *Z. angew. Chem.*, **34**, 266 (1921); F. Eisenlohr and L. Schulze, *Ber.*, **57**, 1808 (1925); F. Eisenlohr, *Fortschr. Chem., Physik u. physik. Chem.*, **18**, 521 (1925).

[8] K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940); B. C. Vickery and K. G. Denbigh, *ibid.*, **45**, 61 (1949).

[9] E. L. Warrick, THIS JOURNAL, **68**, 2455 (1946).

[10] R. West and E. G. Rochow, *ibid.*, **74**, 2490 (1952).

TABLE I

ATOMIC AND BOND PARAMETERS

| Atomic refractivities | | Bond refractivities | | Atomic refraction constants | | Bond refraction constants | |
|---|---|---|---|---|---|---|---|
| P | 7.970 | P—C | 3.575 | P | 54.36 | P—C | 25.57 |
| O (in P=O) | −1.484 | P—Cl | 8.856 | O (in P=O) | 18.92 | P—Cl | 68.57 |
| S (in P=S) | 6.865 | P—H | 4.010 | S (in P=S) | 51.85 | P—F | 34.98 |
| H (in P—H) | 0.991 | P—O | 3.102 | H (in P—H) | −1.57 | P—H | 16.16 |
| | | P=O | −1.032 | | | P—N | 29.28 |
| | | P—S | 7.583 | | | P—O | 28.11 |
| | | P=S | 6.866 | | | P=O | 22.17 |
| | | | | | | P—S | 47.07 |
| | | | | | | P=S | 54.26 |

TABLE II (ABBREVIATED)[a]

| | | | Lorenz–Lorentz molar reactivity $MR_L = \frac{n^2-1}{n^2+2} \times \frac{M}{d}$ | | | Eisenlohr molar refraction product $MR_E = Mn^{20}_D$ | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Calcd. from refractivities | | | Calcd. from refraction constants | |
| No. | Compound | Reference | Obsd. | Atomic | Bond | Obsd. | Atomic | Bond |
| 1 | $PCl_3$ | 3 | 26.154 | 25.502 | 26.568 | 207.75 | 205.59 | 205.72 |
| 2 | $C_2H_5PCl_2$ | 12 | | | | 195.77 | 193.90 | 194.93 |
| 6 | $(C_2H_5O)_2PCl$ | 36 | 38.017 | 37.628 | 37.332 | 224.66 | 227.03 | 224.12 |
| 8 | $(C_4H_9)_2PH$ | 15 | | | | 213.06 | 212.41 | 214.12 |
| 11 | $(C_2H_5)_2POC_3H_7$ | 4d | 45.506 | 45.142 | 45.388 | 212.87 | 213.46 | 213.94 |
| 21 | $C_3H_7P(OC_2H_5)_2$ | 4d | 46.737 | 46.749 | 46.375 | 234.38 | 235.87 | 233.93 |
| 27 | $(C_2H_5O)_3P$ | 14b | 42.822 | 43.961 | 42.714 | 234.87 | 237.75 | 233.32 |
| 31 | $(C_2H_5S)_3P$ | 17 | | | | 336.74 | 329.10 | 336.37 |
| 35 | $(C_2H_5O)_2P\overline{NCH_2CH_2OCH_2CH_2}$ | 18 | | | | 302.36 | 305.76 | 305.45 |
| 43 | $(i\text{-}C_4H_9O)_2P(O)H$ | 14c | 50.330 | 49.931 | 50.046 | 275.78 | 275.61 | 276.28 |
| 52 | $(i\text{-}C_3H_7O)_2P(S)H$ | 5a | 48.700 | 48.990 | 48.648 | 264.98 | 267.36 | 267.17 |
| 56 | $(ClCH_2)(C_6H_5)P(O)OC_2H_5$ | 4c | 54.561 | 54.243 | 54.726 | 333.96 | 327.44 | 238.99 |
| 58 | $C_2H_5P(O)(OC_2H_5)_2$ | 14a | 40.640 | 40.600 | 40.695 | 235.37 | 234.26 | 235.50 |
| 62 | $CH_2{=}CHCHOHP(O)(OCH_3)_2$ | 22 | 37.156 | 37.012 | 37.013 | 242.12 | 239.12 | 240.43 |
| 67 | $CH_3CH{=}CHCHOHP(O)(OC_2H_5)_2$ | 22 | 51.379 | 50.953 | 50.957 | 303.04 | 300.89 | 302.23 |
| 70 | $(CH_3)_2C{=}CH(CH_3)OHP(O)(OC_4H_9)_2$ | 22 | 77.013 | 78.751 | 78.845 | 422.17 | 424.55 | 425.83 |
| 74 | $CH_3C(O)CH_2CH(CH_3)P(O)(OC_4H_9)_2$ | 22 | 73.638 | 73.206 | 73.369 | 401.13 | 400.14 | 401.46 |
| 82 | $(ClCH_2CH_2O)_2P(O)Cl$ | 25 | 46.421 | 45.820 | 45.968 | 355.95 | 351.69 | 352.15 |
| 83 | $(C_2H_5O)_2P(S)Cl$ | 5a, 32 | 44.259 | 44.493 | 44.198 | 277.35 | 278.88 | 278.38 |
| 88 | $CH_3OP(S)(F)Cl$ | 26 | | | | 214.31 | 219.00 | 214.99 |
| 98 | $(C_2H_5)_2N(i\text{-}C_3H_7O)P(S)F$ | 27 | | | | 308.84 | 311.22 | 310.33 |
| 102 | $(i\text{-}C_3H_7O)_2P(S)SH$ | 5b | 56.959 | 56.756 | 57.021 | 319.68 | 319.13 | 321.87 |
| 108 | $(C_4H_9O)_3P{=}O$ | 6e | 69.729 | 70.062 | 69.570 | 379.51 | 379.94 | 379.09 |
| 113 | $(C_3H_7O)_3P{=}S$ | 29 | 63.482 | 64.577 | 63.524 | 348.50 | 351.19 | 349.38 |
| 120 | $(C_2H_5O)_2P(S)SC_2H_5$ | 5b | 56.559 | 56.870 | 57.211 | 321.71 | 320.05 | 321.93 |
| 124 | $(C_2H_5S)_3P{=}S$ | 31 | | | | 399.23 | 380.95 | 390.63 |
| 129 | $(C_5H_{11}O)_2P(O)NHC_6H_5$ | 20 | | | | 464.12 | 470.57 | 465.73 |
| 134 | $(i\text{-}C_4H_9O)_2P(S)SC(O)CH_3$ | 5b | 76.561 | 75.621 | 75.941 | 424.55 | 423.52 | 425.98 |
| 137 | $(C_2H_5O)_2P(S)SC(O)OC_3H_7$ | 5b | 68.708 | 67.743 | 68.099 | 407.98 | 405.40 | 406.84 |
| 150 | $(i\text{-}C_3H_7O)_2P(O)OP(O)(OC_4H_9)_2$ | 34 | | | | 533.65 | 536.13 | 535.24 |

[a] A more complete table, with many more examples, has been deposited as Document number 5631 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance $1.25 for photoprints or $1.25 for 35 mm. microfilm, payable to: Chief, Photoduplication Service, Library of Congress.

relative merits, in their application to phosphorus compounds, of four systems of correlation, *viz.*, two utilizing refractivities (atomic and bond) based on Lorenz–Lorentz molar refractivity, and two utilizing refraction constants (atomic and bond) based on Eisenlohr molar refraction product. For elements other than phosphorus, atomic and bond values from Vogel's tables[6a,6b] have been used in this work. Atomic and bond values for phosphorus and special atomic values for =O, =S and —H in combination with phosphorus were computed[11] by the least squares method from literature data on 150 representative phosphorus compounds,

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[11] The author is indebted to Mr. A. M. Schneider of the Mathematical Analysis Group of these laboratories for assistance and advice in the numerical part of this work.

[12] R. B. Fox, THIS JOURNAL, **72**, 4148 (1950).

[13] P. A. Rossiiskaya and M. I. Kabachnik, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 509 (1947); *C. A.*, **42**, 2924 (1948).

[14] G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, Inc., New York, N. Y., 1950; (a) p. 149; (b) p. 203; (c) p. 202.

[15] N. V. de Bataafsche Petroleum Maatschappij, British Patent 673,451; *C. A.*, **47**, 5426 (1953).

TABLE III

COEFFICIENTS OF VARIATION (× 100)

| | Refractivity (Lorenz-Lorentz) | Refraction (Eisenlohr) |
|---|---|---|
| Atomic | 7.5 | 3.8 |
| Bond | 3.9 | 1.6 |

TABLE IV

| | | | | | Eisenlohr molar refraction product $MR_E = Mn^{20}_D$ | | |
|---|---|---|---|---|---|---|---|
| No. | Compound | Reference | $M$ | $n^{20}_D$ | Obsd. | Calcd. from bond refraction constants | Dev., % |
| 75 | $(C_2H_5O)(C_6H_5)P(O)Cl$ | 20 | 204.60 | 1.4950 | 305.88 | 307.45 | +0.51 |
| 76 | $(C_2H_5O)(C_6H_5)P(S)Cl$ | 20 | 220.67 | 1.5372 | 339.21 | 339.55 | + .10 |
| 126 | $CH_3CH(CN)OP(O)(OCH_3)_2$ | 23 | 179.12 | 1.4092 | 252.42 | 253.19 | + .30 |
| 127 | $CH_3CH(CN)OP(O)(OC_2H_5)_2$ | 33 | 207.17 | 1.4150* | 293.15 | 294.39 | + .42 |
| 131 | $(C_2H_5O)_2P(S)NHC_6H_5$ | 20 | 245.29 | 1.5260 | 374.31 | 374.22 | − .02 |

including 54 for which there are no published density measurements suitable for calculating molar refractivity. The newly computed parameters are shown in Table II, and the observed molar values are compared in Table I with those calculated in accordance with each of the four systems. Refractive indices measured at temperatures other than 20° have been approximately corrected by means of the coefficient −0.0004 per °C. Such correction is denoted by an asterisk, as is density correction when water at 0° was the original basis of comparison. Attention should be called to the fairly close agreement between Vogel's estimates[6d] and the newly derived bond refractivities for P—O and P═O.

Although mere inspection of the complete Table II suffices for establishing the qualitative superiority of the systems of correlation based on the Eisenlohr product, a quantitative comparison in terms of coefficients of variation[37] is shown in Table III, from which it may be inferred that, for phosphorus compounds at least, the Eisenlohr relation serves better than the Lorenz–Lorentz equation and that bond parameters are more trustworthy than atomic values. Apart from the demonstrated merit of the system based on the combined Eisenlohr and Denbigh concepts, it has the further practical advantages to chemists of arithmetical simplicity and of dispensing with density determinations.

In the case of a few of the individual compounds, serious discrepancies in the molar refraction products calculated from bond refraction constants led to the discovery of literature errors. Thus, the published refractive indices of compounds 75, 76 and 131 are 1.5372, 1.4950 and 1.4950, corresponding to −2.24%, +2.92% and +2.05% deviations, respectively. These discrepancies gave rise to a natural suspicion of clerical error, which was confirmed when Professor Kirch,[38] at the request of the author, kindly checked the original data and reported the corrected values shown in Table IV, which is an excerpt from the complete Table II$^a$. Furthermore, compounds 126 and 127 were first formulated as O,O-dialkyl 1-cyano-1-hydroxyethylphosphonates, $CH_3C(OH)(CN)P(O)(OR)_2$, for which the molar refraction products calculated from bond refraction constants are in error by +3.00% and +2.72% deviations, respectively. Hall, Stephens and Drysdale[39] subsequently have reported that analysis by the proton n.m.r. method leads to the conclusion that compound 127 is diethyl 1-cyanoethyl phosphate, $CH_3CH(CN)OP(O)(OC_2H_5)_2$. The present work confirms this structural revision for both compounds.

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(16) A. E. Arbuzov and K. V. Nikonorov, *Doklady Akad. Nauk S.S.S.R.*, **62**, 75 (1948); *C. A.*, **43**, 1004 (1949).

(17) A. Lippert and E. E. Reid, THIS JOURNAL, **60**, 2371 (1938).

(18) G. W. Anderson, J. Blodinger, R. W. Young and A. D. Welcher, *ibid.*, **74**, 5305 (1952).

(19) R. W. Young, *ibid.*, **75**, 4620 (1953).

(20) D. Ramaswami and E. R. Kirch, *ibid.*, **75**, 1763 (1953).

(21) M. I. Kabachnik, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 233 (1947); *C. A.*, **42**, 4132 (1948).

(22) A. N. Pudovik, *Doklady Akad. Nauk S.S.S.R.*, **73**, 499 (1950); *C. A.*, **45**, 2856 (1951).

(23) M. I. Kabachnik, P. A. Rossiiskaya and E. S. Shepeleva, *Bull. acad. sci. U.R.S.S., Classe sci. chim.*, 163 (1947); *C. A.*, **42**, 4133 (1948).

(24) W. Gerrard, *J. Chem. Soc.*, 1466 (1940).

(25) M. I. Kabachnik and P. A. Rossiiskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 403 (1946); *C. A.*, **42**, 7242 (1948).

(26) G. Ohláh and A. Oswald, *Ann.*, **602**, 118 (1957).

(27) G. Ohláh, A. Oswald and A. Mlinko, *ibid.*, **602**, 123 (1957).

(28) W. G. Emmett and H. O. Jones, *J. Chem. Soc.*, **99**, 716 (1911).

(29) B. A. Arbuzov and T. G. Shavsha, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 795 (1951); *C. A.*, **46**, 3817 (1952).

(30) V. P. Wystrach, private communication.

(31) K. C. Brannock, THIS JOURNAL, **73**, 4954 (1951).

(32) J. H. Fletcher, J. C. Hamilton, I. Hechenbleikner, E. I. Hoegberg, B. J. Sertl and J. T. Cassaday, *ibid.*, **70**, 3944 (1948).

(33) L. A. R. Hall and C. W. Stephens, *ibid.*, **78**, 2567 (1956).

(34) A. D. F. Toy, *ibid.*, **72**, 2065 (1950).

(35) A. E. Arbuzov and B. A. Arbuzov, *J. prakt. Chem.*, [2] **130**, 123 (1931).

(36) A. E. Arbuzov and B. A. Arbuzov, *Ber.*, **65**, 196 (1908).

(37) The coefficient of variation is a measure of precision obtained by dividing the standard deviation of a set of measurements by the mean value of the measurements. It decreases as the precision increases.

(38) E. R. Kirch, private communication.

(39) L. A. R. Hall, C. W. Stephens and J. J. Drysdale, THIS JOURNAL, **79**, 1768 (1957).