Physical Property Correlations for Conjugated Aliphatic Nitro-olefins

Refractive Index, Density, and Boiling Point

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THE EFFECT of the conjugated nitro-olefin group on various physical properties has been determined. The boiling points at 10 mm. and the refractive indices and densities at 30°, 40°, and 60° C. were measured for a series of 21 conjugated linear nitro-olefins having straight-chain alkyl groups ranging from methyl to hexyl substituted on each carbon of nitroethylene. From this, in conjunction with selected literature values, equations are developed which correlate structure with boiling point, molar volume, density, refractive index, molar refraction, dispersion, Abbe number, n–d intercept, and refractive index and density-temperature coefficients.

Although a number of compounds containing a conjugated nitro-olefin group have been reported in the literature, only boiling points, refractive indices, or densities have been measured, and virtually no attempt has been made to correlate these properties with the structures of these compounds.

EXPERIMENTAL

Preparation and Boiling Point. The nitroalcohols and their acetates were prepared by the method of Vanderbilt and Hass (*27*). The nitro-olefins were prepared by removing the elements of acetic acid from the nitroacetates by heating them with 2 grams per mole of anhydrous sodium acetate for 4 to 6 hours at 115° to 120° C., followed by distillation in vacuo. The crude nitro-olefin was then mixed with benzene to avoid emulsion formation, washed successively with brine, sodium bicarbonate solution, and again with brine, dried over sodium sulfate, and fractionated in vacuo through a column with a minimum of 60 theoretical plates. The boiling point was obtained by redistilling this fraction and observing the boiling point within the middle third under total reflux at 10 mm.

From infrared evidence, these compounds are believed to be all or wholly in the trans configuration.

The conjugated nitro-olefins are relatively unstable compounds which readily undergo polymerization, particularly in the presence of alkali or water. Traces of alkali are also capable of inducing a tautomeric shift of the double bond to the beta-gamma nonconjugated isomer (*26*). Although efforts were made to minimize these changes, they undoubtedly have affected the final results to some extent.

The elemental analysis was done elsewhere. The analyst reported difficulty in obtaining reproducible results with duplicates of the same sample.

Density. The densities were determined in stoppered density bulbs by the method of MacKenzie, Mills, and Scott (*18*), a cathetometer being used for the measurements.

Refractive Index. The refractive indices were measured with an Abbe refractometer connected to a thermostat. The dispersion was measured with the Abbe refractometer using a mercury lamp.

The experimental data are listed in Table I.

In addition to the compounds measured in this research, literature values from the following were utilized in developing the correlations.

Compd. No.	Compd. Name	Compd. No.	Compd. Name
22	Nitroethylene	35	4-Methyl-3-nitro-2-pentene
23	1-Nitropropene	36	2,3-Dimethyl-1-nitro-1-butene
24	2-Nitropropene	37	1-Nitro-1-heptene
25	1-Nitro-1-butene	38	2-Nitro-1-heptene
26	2-Nitro-1-butene	39	5-Methyl-3-nitro-3-hexene
27	2-Methyl-1-nitro-1-propene	40	1-Nitro-1-octene
28	1-Nitro-1-pentene	41	2-Methyl-3-nitro-3-heptene
29	2-Nitro-1-pentene	42	4-Ethyl-2-nitro-2-hexene
30	3-Methyl-1-nitro-1-butene	43	5-Ethyl-3-nitro-3-heptene
31	1-Nitro-1-hexene	44	3-Nitro-3-decane
32	2-Nitro-1-hexene	45	4-Ethyl-3-nitro-2-Octene
33	4-Methyl-1-nitro-1-pentene	46	5-Ethyl-3-nitro-3-nonene
34	4-Methyl-2-nitro-2-pentene		

RESULTS AND DISCUSSION

Boiling Points. The equation of Egloff, Sherman, and Dull (*8*) was chosen as the basis for correlating the boiling points of the nitro-olefins. For the structure $R_AR_CC=C(NO_2)R_B$,

$$b_{10} = A \log(n + 4.4) + B \quad (1)$$

where n = number of C atoms, was utilized for $R_A >$ ethyl, $R_B >$ ethyl, and R_C = H. The following constants were obtained by fitting the b_{10}'s of the 21 compounds listed in Table I by the method of least squares: A = 362.1, B = −301.4, corr. (R_A = Me) = +4.8°, corr. (R_A = Et) = +1.4°, corr. (R_B = Me) = +10.5°, corr. (R_B = Et) = +2.5°. This equation, with correction constants, fits the values in Table I with a 50% probable error of 0.7°.

The system of Cragoe, Hass, and Newton (*31*) was chosen for the estimation of boiling points at other pressures. Fits of available data on nitro-olefins indicate a class between group 3 and group 4, represented by the equation

$$\Phi = 4.90 + 0.00216\, b_{760} \quad (2)$$

This equation in conjunction with the equation

$$T_p/T_{760} = [\Phi + 0.15 \log (760/P)]/[\Phi + 1.15 \log (760/P)] \quad (3)$$

where T_p and T_{760} = b.p.'s (° K.) at P mm. and 760 mm., respectively, allows the estimation of b_{760}'s and b_{10}'s from literature data at other pressures. The following additional correction constants were calculated using literature data converted to b_{10}: corr. (R_B = H) = +18.2° (from compounds 23, 25, 28, and 40), corr. (R_A = H) = −9.1° (from compounds 22, 24, 26, 29, and 38), corr. (R_A or R_B = secondary alkyl group) = −9.4° (from compounds 30, 34, 35, and 41), and corr. (R_C = Me) = −3.7° (from compounds 27 and 36). Only boiling points at pressures above 5 mm. were considered.

Table I. Physical Properties and Analyses

Compd. No.	Compd. Name	B.P. (10 Mm.)	n'_D 30°	n'_D 40°	n'_D 60°	$-\Delta n_D/\Delta t \times 10^4$	Disp. $n_F - n_C \times 10^2$	d'_4 30°	d'_4 40°	d'_4 60°	$-\Delta d/\Delta t \times 10^3$	Analyses, % Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N	Lit. Ref.
1	2-Nitro-2-butene	49.1	1.4544	1.4495	1.4400	4.80	1.70	1.0374	1.0263	1.0057	1.057	47.52	6.98	13.85	47.63	6.95	14.17	[a, b, c, d]
2	2-Nitro-2-pentene	64.4	1.4496	1.4449	1.4354	4.72	1.51	0.9972	0.9872	0.9672	1.000	52.16	7.88	12.17	53.37	8.17	11.85	
3	3-Nitro-2-pentene	59.3	1.4513	1.4464	1.4370	4.79	1.48	1.0031	0.9932	0.9734	0.990	52.16	7.88	12.17	52.26	7.89	11.94	[a, d]
4	2-Nitro-2-hexene	75.6	1.4580	1.4533	1.4444	4.56	1.49	0.9798	0.9700	0.9518	0.930	55.79	8.58	10.85	55.15	8.50	10.83	[a, d, e, f]
5	3-Nitro-2-hexene	70.9	1.4545	1.4497	1.4412	4.54	1.52	0.9797	0.9701	0.9518	0.935	55.79	8.58	10.85	56.36	8.72	10.84	[a]
6	3-Nitro-3-hexene	70.6	1.4510	1.4464	1.4374	4.54	1.48	0.9739	0.9651	0.9458	0.927	55.79	8.58	10.85	54.68	8.59	10.58	[e, f]
7	2-Nitro-2-heptene	91.3	1.4579	1.4533	1.4446	4.46	1.49	0.9598	0.9509	0.9334	0.876	58.72	9.15	9.78	59.23	8.94	9.79	
8	3-Nitro-2-heptene	86.0	1.4528	1.4481	1.4395	4.44	1.34	0.9631	0.9539	0.9363	0.893	58.72	9.15	9.78	58.81	9.16	9.26	
9	3-Nitro-3-heptene	82.5	1.4508	1.4461	1.4375	4.51	1.35	0.9568	0.9473	0.9293	0.917	58.72	9.15	9.78	58.71	9.30	9.44	[a]
10	4-Nitro-3-heptene	81.5	1.4549	1.4503	1.4410	4.53	1.44	0.9572	0.9480	0.9300	0.910	58.72	9.15	9.78	58.34	8.96	9.70	[g]
11	2-Nitro-2-octene	105.6	1.4558	1.4515	1.4429	4.28	1.37	0.9449	0.9363	0.9189	0.868	61.12	9.62	8.91	60.51	9.16	7.72	
12	3-Nitro-2-octene	100.1	1.4527	1.4485	1.4400	4.18	1.32	0.9452	0.9366	0.9196	0.854	61.12	9.62	8.91	61.09	9.15	8.85	
13	3-Nitro-3-octene	98.0	1.4567	1.4524	1.4438	4.37	1.44	0.9460	0.9370	0.9198	0.860	61.12	9.62	8.91	60.98	9.64	8.40	
14	4-Nitro-3-octene	96.1	1.4523	1.4478	1.4392	4.39	1.33	0.9412	0.9324	0.9155	0.861	61.12	9.62	8.91	61.07	9.53	8.36	
15	4-Nitro-4-octene	95.1	1.4560	1.4514	1.4427	4.46	1.41	0.9451	0.9363	0.9188	0.875	61.12	9.62	8.91	61.01	9.56	9.11	[a]
16	2-Nitro-2-nonene	116.9	1.4516	1.4472	1.4388	4.27	1.24	0.9298	0.9214	0.9050	0.829	63.13	10.01	8.18	62.73	9.74	7.18	
17	3-Nitro-2-nonene	110.1	1.4543	1.4500	1.4417	4.24	1.29	0.9357	0.9271	0.9110	0.827	63.13	10.10	8.18	62.60	9.74	8.03	
18	3-Nitro-3-nonene	109.0	1.4526	1.4482	1.4399	4.28	1.30	0.9303	0.9220	0.9056	0.825	63.13	10.01	8.18	63.31	9.90	8.23	
19	4-Nitro-3-nonene	108.0	1.4489	1.4447	1.4363	4.20	1.22	0.9269	0.9186	0.9018	0.836	63.13	10.01	8.18	63.10	9.95	7.69	
20	4-Nitro-4-nonene	108.7	1.4571	1.4524	1.4442	4.37	1.34	0.9338	0.9251	0.9082	0.852	63.13	10.01	8.18	63.41	10.15	8.13	
21	5-Nitro-4-nonene	107.6	1.4537	1.4493	1.4405	4.38	1.30	0.9305	0.9220	0.9053	0.884	63.13	10.01	8.18	63.91	9.87	8.17	

[a] (*11*) Cpd. 1 (b_{30} 70.4°, $n^{25}D$ 1.4584, d_4^{25} 1.0429), Cpd. 3 (b_{10} 57.8°, $n^{25}D$ 1.4590, d_4^{25} 1.0069), Cpd. 4 (b_{10} 82.3°, $n^{25}D$ 1.4572, d_4^{25} 0.9824), Cpd. 5 (b_{10} 72.0°, $n^{25}D$ 1.4572, d_4^{25} 0.9833), Cpd. 9 (b_{10} 84.4°, $n^{25}D$ 1.4580, d_4^{25} 0.9625), Cpd. 15 (b_{10} 93.0°, $n^{25}D$ 1.4593, d_4^{25} 0.9484).
[b] (*15*) Cpd. 1 (b_{15} 55.5°, $n^{22}D$ 1.4600).
[c] (*3*) Cpd. 1 (b_9 47–50°, $n^{19}D$ 1.4616).
[d] (*13*) Cpd. 1 (b_{30} 70°, $n^{20}D$ 1.4585), Cpd. 3 (b_{10} 58° $n^{20}D$ 1.4534), Cpd. 4 (b_{10} 82°, $n^{20}D$ 1.4530).
[e] (*19*) Cpd. 4 (b_1 53°, $n^{25}D$ 1.4513, d_4^{25} 0.9883), Cpd. 6 (b_1 53°, n_4^{25} 1.4521, d_4^{25} 0.9785).
[f] (*21*) Cpd. 4 (b_4 60–2°, $n^{25}D$ 1.4536, Cpd. 6 (b_{25} 85–7°, $n^{25}D$ 1.4538).
[g] (*25*) Cpd. 10 ($b_{5.2}$ 70.0–70.8°, $n^{20}D$ 1.4585).

The calculations and results are summarized in Table II.

Molar Volume and Density. The molar volume equation of Li and others (*17*) was modified by replacing m, the number of carbons in the normal alkyl chains, by n, the total number of carbons. For the structure $R_AR_CC=C(NO_2)R$ the equation

$$V_{25}\text{ (ml. per mole)} = A + 16.484n + B/n + C/n^2 \quad (4)$$

was utilized for $n > 3$, $R_A >$ ethyl, $R_B >$ ethyl, and R_C = H. The following constants were obtained by fitting the V_{25}'s of the 21 compounds listed in Table I by the method of least squares: A = 42.55, B = −94.40, C = 198.78, corr. (R_A = Me) = −0.24, corr. (R_A = Et) = +0.67, corr. (R_B = Me) = +0.17, corr. (R_B = Et) = +0.30. This equation, with correction constants, fits the V_{25}'s of the 21 compounds with a 50% probable error of 0.21 ml. per mole.

$\Delta d/\Delta t$ varied nearly linearly with density, giving, by least squares fit,

$$\Delta d/\Delta t = 0.001136 - 0.002110\, d_4^{25} \quad (5)$$

This equation fitted the experimental values of $\Delta d/\Delta t$ with a 50% probable error of 9×10^{-6}. It is equivalent to

$$d_4' = 1.0528 d_4^{25} - 0.0284 + (0.001136 - 0.002110 d_4^{25})t \quad (6)$$

Densities at 30°, 40°, and 60° C. calculated by a combination of Equations 4 and 6 fit the experimental data for the 21 compounds with a 50% probable error of 0.0015. The calculations and results are summarized in Table III.

The following approximate correction values based on literature data were calculated: corr. (R_B = H) = +1.6 (from compounds 25, 28, and 40), corr. (R_A = H) = +2.3 (from 26), corr. (R_C = Me) = −1.2 (from compound 27), and corr. (R_A or R_B = *sec*-alkyl group) = −1.7 (from compounds 39, 42, 43, 45, and 46). There are some major inconsistencies in the literature data. Further experimental work is being carried out in this area.

A formula of the type used in Equation 4 should not be used for extrapolations to values of n less than the smallest value used in the least squares fit. Moderate extrapolation for higher values of n may prove satisfactory.

The calculations and results are summarized in Table III.

Refractive Index and Dispersion. One moderately satisfactory method of estimating the refractive index at 25° C. is through the additivity of group $Mn^{25}D$'s. For the series $R_AR_CC=C(NO_2)R_B$ the following group contributions were obtained by fitting the $Mn^{25}D$'s of the 21 compounds listed in Table I by the method of least squares: $CH=C(NO_2)$ 123.43, R_A = Me 11.64, R_B = Me 11.95, R_A = Et 31.87, R_B = Et 32.21, Pr 53.00, Bu 73.35, Am 93.45, and Hx 113.94. The $n^{25}D$'s estimated by this method fitted the $n^{25}D$'s of the 21 compounds with a 50% probable error of 0.0016. The alkyl group contributions obtained above may be compared to the following values of Vogel (*28*) (converted to 25° C.): Me 11.67, Et 32.94, Pr 52.74, Bu 73.28, Am 93.90, and Hx 114.52.

The following approximate group $Mn^{25}D$ contributions based on literature data were calculated: R_B = H −8.8 (from compounds 23, 25, 31, 37, and 40), R_A = H −10.7 (from compounds 24, 26, and 32), and R_C = Me 22.3 (from compounds 27 and 36). For methyl branching on the alkyl group (R_A or R_B) subtract 0.8 (from compounds 30, 33, 34, 35, 39, and 40); for ethyl branching on the α-carbon of the alkyl group (R_A or R_B) add 1.1 (from compounds 42, 43, 45, and 46). There are some major inconsistencies in the literature data. Further experimental work is being carried out in this area.

$\Delta n_D/\Delta t$ was found to vary nearly linearly with $Mn^{25}D$, and with n, the number of carbons, giving, by least squares fit,

$$\Delta n_D/\Delta t = -5.58 \times 10^{-4} + 5.22 \times 10^{-7} Mn^{25}D \quad (7)$$

and

$$\Delta n_D/\Delta t = -5.17 \times 10^{-4} + 9.7 \times 10^{-6} n \quad (8)$$

Table II. Boiling Points of Conjugated Nitro-Olefins

Compd. No.	Lit. Values, ° C.	Lit. Ref.	b_{10}, ° C. Obsd.	b_{10}, ° C. Eq.	Δb_{10}, Obsd. − Eq.
1		TR[a]	49.1	48 7	+0.4
	b_{30}, 70.4	(*11*)	49.0	48.7	+0.3
	b_{15}, 55.5	(*15*)	48.0	48.7	−0.7
	b_9, 47–50	(*3*)	50.3	48.7	+1.6
	b_{30}, 70	(*13*)	48.6	48.7	−0.1
2		TR	64.4	62.9	+1.5
3		TR	59.3	58.3	+1.0
	b_{10}, 57.8	(*11*)	57.8	58.3	−0.5
	b_{10}, 58	(*13*)	58.0	58.3	−0.3
4		TR	75.6	77.4	−1.8
	b_{10}, 82.3	(*11*)	82.3	77.4	+4.9
	b_{10}, 82	(*13*)	82.0	77.4	+4.6
	b_4, 60–2	(*21*)	73.6	77.4	−3.8
5		TR	70.9	71.7	−0.8
	b_{10}, 72	(*11*)	72.0	71.7	+0.3
6		TR	70.6	70.8	−0.2
	b_{25}, 85–7	(*21*)	67.6	70.8	−3.2
7		TR	91.3	91.9	−0.6
8		TR	86.0	86.2	−0.2
9		TR	82.5	83.9	−1.4
	b_{10}, 84.4	(*11*)	84.4	83.9	+0.5
10		TR	81.5	82.7	−1.2
	$b_{5.2}$, 70.0–70.8	(*25*)	82.6	82.7	−0.1
11		TR	105.6	105.1	+0.5
12		TR	100.1	99.4	+0.7
13		TR	98.0	97.1	+0.9
14		TR	96.1	96.0	+0.1
15		TR	95.1	94.6	+0.5
	b_{10}, 93.0	(*11*)	93.0	94.6	−1.6
16		TR	116.9	117.3	−0.4
17		TR	110.1	111.6	−1.5
18		TR	109.0	109.3	−0.3
19		TR	108.0	108.2	−0.2
20		TR	108.7	106.8	+1.9
21		TR	107.6	106.8	+0.8
22	b_{80}, 38–39	(*6*)	0.8	−0.3	+1.1
	b_{760}, 98.5	(*32*)	2.4	−0.3	+2.7
22	b_{10}, −0.2	(*14*)	−0.2	−0.3	+0.1
23	b_{10}, 37	(*23*)	37.0	36.1	+0.9
	b_7, 31.0–32.5	(*28*)	37.9	36.1	+1.8
24	b_{100}, 57.0	(*11*)	13.0	14.8	−1.8
	b_{90}, 58	(*6*)	16.0	14.8	+1.2
	b_{144}, 68–70	(*3*)	16.0	14.8	+1.2
	$b_{59.5}$, 48–49	(*2*)	15.5	14.8	+0.7
25	b_{12}, 55	(*23*)	51.6	53.0	−1.4
	b_{12}, 57	(*5*)	53.6	53.0	+0.6
26	b_{50}, 60.5	(*11*)	29.8	26.8	+3.0
	b_{17}, 47	(*13*)	37.4	26.8	+10.6
27	b_{25}, 72	(*26*)	54.2	52.7	+1.5
	b_{18}, 64	(*4*)	52.9	52.7	+0.2
	b_{11}, 56	(*16*)	54.2	52.7	+1.5
	$b_{9.5}$, 48–49	(*3*)	49.4	52.7	−3.3
	b_{11}, 55–56	(*13*)	53.7	52.7	+1.0
28	b_9, 66.5	(*5*)	68.5	69.2	−0.7
	b_{12}, 69–70	(*23*)	66.1	69.2	−3.1
	b_{12}, 69–70	(*13*)	66.1	69.2	−3.1
29	b_{20}, 58	(*11*)	41.1	41.9	−0.8
	b_{50}, 68	(*1*)	36.7	41.9	−5.2
30	b_{23}, 75	(*13*)	58.7	59.8	−1.1
32	b_{50}, 81–2	(*13*)	49.1	57.8	−8.7
33	b_{12}, 81–2	(*1*)	78.0	85.1	−7.1
34	b_{10}, 67	(*13*)	67.0	70.6	−3.6
35	b_{10}, 64	(*11*)	64.0	62.3	+1.7
36	b_{10}, 76.0–6.2	(*5*)	76.1	73.6	+2.5
38	b_{30}, 93.5	(*1*)	70.9	72.3	−1.4
40	b_9, 112	(*23*)	114.2	112.8	+1.4
41	b_{10}, 85.5	(*11*)	85.5	85.2	+0.3

[a] This research.

Equations 7 and 8 fitted the experimental values of $\Delta n_D/\Delta t$ with 50% probable errors of 0.05×10^{-4} and 0.05×10^{-4}, respectively.

The dispersion ($n_F - n_C$) was found to vary nearly linearly with $Mn^{25}D$, and with n, the number of carbons, giving, by least squares fit,

$$n_F - n_C = 0.0208 - 3.2 \times 10^{-5} Mn^{25}D \quad (9)$$

and

$$n_F - n_C = 0.0188 - 6.5 \times 10^{-4} n \quad (10)$$

Table III. Densities of Conjugated Nitro-olefins

Compd., No.	$-\Delta d/\Delta t \times 10^4$ Eq. 5	$-\Delta d/\Delta t \times 10^4$ Obsd.	Obsd.-Eq. $\times 10^4$	V_{25}, Eq. 4	d_4^{25}, Eqs.	Lit. Ref.	t, ° C.	d_4^t Eq. 6	d_4^t Obsd. or lit.	Δd_4^t, Obsd. – Eq. or Lit. – Eq.
1	10.64	10.57	−0.07	97.11	1.0411	TR	30.0	1.0358	1.0374	+0.0016
				97.11	1.0411	(11)	25.0	1.0411	1.0429	+0.0018
2	9.79	10.00	+0.21	114.77	1.0032	TR	30.0	0.9983	0.9972	−0.0011
3	9.91	9.90	−0.01	114.00	1.0100	TR	30.0	1.0050	1.0031	−0.0019
				114.00	1.0100	(11)	25.0	1.0100	1.0069	−0.0031
4	9.40	9.30	−0.10	131.32	0.9836	TR	30.0	0.9789	0.9798	+0.0009
				131.32	0.9836	(11)	25.0	0.9836	0.9824	−0.0012
				131.32	0.9836	(19)	25.0	0.9836	0.9883	+0.0047
5	9.41	9.35	−0.06	130.92	0.9866	TR	30.0	0.9819	0.9797	−0.0022
				130.92	0.9866	(11)	25.0	0.9866	0.9833	−0.0033
6	9.29	9.27	−0.02	132.12	0.9776	TR	30.0	0.9730	0.9739	+0.0009
				132.12	0.9776	(19)	25.0	0.9776	0.9785	+0.0009
7	8.98	8.76	−0.22	148.60	0.9636	TR	30.0	0.9591	0.9598	+0.0007
8	9.05	8.93	−0.22	148.20	0.9662	TR	30.0	0.9617	0.9631	+0.0014
9	8.92	9.17	+0.25	148.73	0.9628	TR	30.0	0.9583	0.9568	−0.0015
				148.73	0.9628	(11)	25.0	0.9628	0.9628	0.0000
10	8.93	9.10	+0.17	149.10	0.9604	TR	30.0	0.9560	0.9572	+0.0012
11	8.67	8.68	+0.01	165.83	0.9481	TR	30.0	0.9438	0.9449	+0.0011
12	8.67	8.54	−0.13	165.42	0.9504	TR	30.0	0.9461	0.9452	−0.0009
13	8.68	8.60	−0.08	165.96	0.9473	TR	30.0	0.9430	0.9460	+0.0030
14	8.59	8.61	+0.02	166.33	0.9452	TR	30.0	0.9409	0.9412	+0.0003
15	8.67	8.75	+0.08	165.66	0.9491	TR	30.0	0.9448	0.9451	+0.0003
				165.66	0.9491	(11)	25.0	0.9491	0.9484	−0.0007
16	8.35	8.29	−0.06	182.98	0.9358	TR	30.0	0.9316	0.9298	−0.0018
17	8.47	8.27	−0.20	182.57	0.9379	TR	30.0	0.9337	0.9357	+0.0020
18	8.36	8.25	−0.11	183.11	0.9352	TR	30.0	0.9310	0.9303	−0.0007
19	8.25	8.36	+0.11	183.48	0.9333	TR	30.0	0.9291	0.9269	−0.0022
20	8.43	8.52	+0.09	182.72	0.9372	TR	30.0	0.9330	0.9338	+0.0008
21	8.36	8.44	+0.08	182.72	0.9372	TR	30.0	0.9330	0.9305	−0.0025
25	...	...	...	99.45	1.0167	(23)	20.0	1.0217	1.0251	+0.0034
26	...	...	...	99.78	1.0133	(22)	20.0	1.0183	1.0188	+0.0005
27	...	...	...	97.34	1.0387	(26)	20.0	1.0440	1.0438	−0.0002
28	...	...	...	115.54	0.9965	(23)	20.0	1.0013	0.9952	−0.0061
34	...	...	...	129.62	0.9965	(11)	25.0	0.9965	0.9780	−0.0185
37	...	...	...	150.04	0.9543	(19)	25.0	0.9543	0.9743	+0.0200
39	...	...	...	147.04	0.9738	(19)	25.0	0.9738	0.9741	+0.0003
40	...	...	...	167.26	0.9400	(23)	20.0	0.9442	0.9476	+0.0034
42	...	...	...	164.13	0.9579	(19)	25.0	0.9579	0.9551	−0.0028
43	...	...	...	181.41	0.9439	(19)	25.0	0.9439	0.9427	−0.0012
44	...	...	...	200.18	0.9255	(19)	25.0	0.9255	0.9235	−0.0020
45	...	...	...	198.35	0.9341	(19)	25.0	0.9341	0.9343	+0.0002
46	...	...	...	215.49	0.9249	(19)	25.0	0.9249	0.9273	+0.0024

Equations 9 and 10 both fitted the experimental values of $n_F - n_C$ with a 50% probable error of 4×10^{-4}.

The calculations and results are summarized in Table IV.

Molar Refraction. By using Vogel's (*29*) values of bond and group refractions at 20° (Me 5.00, Et 9.65, Pr 14.32, Bu 18.94, Am 23.60, Hx 28.21, C—H 1.676, C—C 1.296), an average value of 12.19 for the group (C=C—NO_2) was obtained. This yields an "exhaltation" of 0.67 as compared to the group value obtained from NO_2 5.78 (calculated from Vogel's values for seven nitroalkanes), C=C 4.17 and C—N 1.57. The molar refractions estimated by this method fitted the molar refractions of the 21 compounds with a 50% probable error of 0.11.

The molar refractions of these compounds were found to increase an average of 0.0076% per degree.

The equation of Kurtz and Ward (*14*), $n_D = (d/2) + b$, was examined. The b term was found to vary appreciably over the series and was fitted by least squares to the equations

$$b = a + [c/(n+1)] \quad (11)$$

and

$$b = [ac^n]^{1/(n+1)} \quad (12)$$

where n is the number of carbons. These yielded the over-all equations

$$n^{25}D = \frac{d_4^{25}}{2} + 1.0432 - \frac{0.549}{n+1} \quad (13)$$

and

$$n^{25}D = \frac{d_4^{25}}{2} + [(0.6035)(1.0436)^n]^{1/(n+1)} \quad (14)$$

For both of these equations, $n^{25}D$'s calculated from experimental d_4^{25}'s fitted the experimental $n^{25}D$'s of the 21 compounds with a 50% probable error of 0.0014. This is the same as the probable error obtained for $n^{25}D$'s calculated by using the molar refractions.

These calculations and results are summarized in Table V, along with similar calculations using literature data.

The ratio of $\Delta d/\Delta t$ to $(\Delta n_D/\Delta t)^2$ was found to be constant and equal to -4.52×10^3 with a 50% probable error of 0.09×10^3. Combining this result with Equation 8 gives

$$\Delta d/\Delta n_D = 2.34 - 0.044n \quad (15)$$

where n is the number of carbon atoms. This may be compared to the constant value of 1.67 for $\Delta d/\Delta n_D$ estimated by Ward and Kurtz (*30*).

The "Abbe number," $\nu = (n_D - 1)/(n_F - n_C)$, ranged from 27.0 to 36.7, about the same range as for the conjugated dienes, but well below that for either the unconjugated dienes or nitroalkanes, each of which range upward from about 40. The Abbe number was fitted by least squares to the following equations:

$$\nu = 22.2 + 1.45n \quad (16)$$

and

$$\nu = 42.8 - \frac{80.6}{n+1} \quad (17)$$

These two equations fitted the experimental ν's equally well with a 50% probable error of 0.7. For extrapolation to higher values of $n(>9)$ use Equation 17; for extrapolation to lower values of $n(<4)$ use Equation 16.

Results are summarized in Table VI.

Table IV. Refractive Indices and Dispersions of Nitro-olefins

Compd., No.	$-\Delta n_D/\Delta t \times 10^4$ Eq. 7	Eq. 8	Obsd.	$n_F - n_C \times 10^2$ Eq. 9	Eq. 10	Obsd.	$n^{25}D$, Est.	Lit. Ref.	t, °C.	$n'D$ Est.	Obsd.	$\Delta n'D$ Obsd. – Est.
1	4.81	4.78	4.80	1.61	1.62	1.70	1.4541	TR	30.0	1.4517	1.4544	+0.0027
								(11)	25.0	1.4541	1.4584	+0.0043
								(15)	22.0	1.4555	1.4600	+0.0045
								(3)	19.0	1.4570	1.4616	+0.0036
								(13)	20.0	1.4565	1.4585	+0.0020
2	4.71	4.68	4.72	1.54	1.56	1.51	1.4526	TR	30.0	1.4502	1.4496	−0.0006
3	4.71	4.68	4.79	1.54	1.56	1.48	1.4528	TR	30.0	1.4504	1.4513	+0.0009
								(11)	25.0	1.4528	1.4590	+0.0062
								(13)	20.0	1.4552	1.4534	−0.0018
4	4.60	4.59	4.56	1.48	1.49	1.49	1.4585	TR	30.0	1.4562	1.4580	+0.0018
								(11)	25.0	1.4585	1.4572	−0.0013
								(19)	25.0	1.4585	1.4513	−0.0072
								(21)	25.0	1.4585	1.4536	−0.0049
								(13)	20.0	1.4608	1.4530	−0.0078
5	4.60	4.59	4.54	1.48	1.49	1.52	1.4561	TR	30.0	1.4538	1.4545	+0.0007
								(11)	25.0	1.4561	1.4572	+0.0011
6	4.60	4.59	4.54	1.48	1.49	1.48	1.4517	TR	30.0	1.4494	1.4510	+0.0016
								(19)	25.0	1.4517	1.4521	+0.0004
								(21)	25.0	1.4517	1.4538	+0.0021
7	4.49	4.49	4.46	1.41	1.42	1.49	1.4577	TR	30.0	1.4555	1.4579	+0.0024
8	4.49	4.49	4.44	1.41	1.42	1.34	1.4556	TR	30.0	1.4534	1.4528	−0.0006
9	4.49	4.49	4.51	1.41	1.42	1.35	1.4570	TR	30.0	1.4548	1.4508	−0.0040
								(11)	25.0	1.4570	1.4580	+0.0010
10	4.49	4.49	4.53	1.41	1.42	1.44	1.4571	TR	30.0	1.4549	1.4549	0.0000
								(25)	20.0	1.4593	1.4585	−0.0008
11	4.39	4.39	4.28	1.35	1.36	1.37	1.4555	TR	30.0	1.4533	1.4558	+0.0025
12	4.38	3.39	4.18	1.35	1.36	1.32	1.4535	TR	30.0	1.4513	1.4527	+0.0012
13	4.39	4.39	4.37	1.35	1.36	1.44	1.4564	TR	30.0	1.4542	1.4567	+0.0025
14	4.39	4.39	4.39	1.35	1.36	1.33	1.4565	TR	30.0	1.4543	1.4523	−0.0020
15	4.38	4.39	4.46	1.35	1.36	1.41	1.4593	TR	30.0	1.4571	1.4560	−0.0011
								TR	25.0	1.4593	1.4593	0.0000
16	4.28	4.30	4.27	1.28	1.30	1.24	1.4560	(11)	30.0	1.4539	1.4516	−0.0023
17	4.29	4.30	4.24	1.28	1.30	1.29	1.4542	TR	30.0	1.4521	1.4543	+0.0022
18	4.29	4.30	4.28	1.28	1.30	1.30	1.4546	TR	30.0	1.4525	1.4526	+0.0001
19	4.29	4.30	4.20	1.28	1.30	1.22	1.4546	TR	30.0	1.4525	1.4489	−0.0036
20	4.28	4.30	4.37	1.28	1.30	1.34	1.4587	TR	30.0	1.4566	1.4571	+0.0005
21	4.28	4.30	4.38	1.28	1.30	1.30	1.4587	TR	30.0	1.4566	1.4537	−0.0029
22	...	...	...	...	...	...	14.227	TR	25.0	1.4227	1.4254	0.0027
23							1.4499	(3)	19.0	1.4528	1.4663	+0.0135
							1.4499	(23)	20.0	1.4524	1.4527	+0.0003
								(22)	20.0	1.4524	1.4539	+0.0015
24							1.4316	(11)	25.0	1.4316	1.4105	−0.0211
								(2)	23.0	1.4326	1.4292	−0.0031
								(3)	22.0	1.4331	1.4309	−0.0022
								(23)	20.0	1.4341	1.4527	+0.0186
								(9)	20.0	1.4341	1.4296	−0.0045
25							1.4489	(5)	20.0	1.4513	1.4560	+0.0047
								(23)	20.0	1.4513	1.4532	+0.0019
26							1.4335	(24)	20.0	1.4359	1.4360	+0.0001
								(13)	20.0	1.4359	1.4325	−0.0034
								(1)	20.0	1.4359	1.4356	−0.0003
								(22)	20.0	1.4359	1.4373	+0.0014
								(9)	20.0	1.4359	1.4258	−0.0101
27							1.4694	(26)	20.0	1.4718	1.4710	−0.0008
								(13, 16)	20.0	1.4718	1.4680	−0.0038
								(4)	20.0	1.4718	1.4702	−0.0016
								(10)	17.0	1.4732	1.4723	−0.0009
28							1.4559	(5)	20.0	1.4582	1.4580	−0.0002
								(13)	20.0	1.4582	1.4518	−0.0064
								(23)	20.0	1.4582	1.4550	−0.0032
30							1.4489	(13)	20.0	1.4512	1.4487	−0.0025
31							1.4554	(7)	25.0	1.4554	1.4531	−0.0023
32							1.4406	(1)	20.0	1.4429	1.4462	+0.0033
33							1.4492	(13)	20.0	1.4515	1.4514	−0.0001
34							1.4523	(19)	25.0	1.4523	1.4520	−0.0003
								(13)	20.0	1.4546	1.4524	−0.0022
35							1.4499	(11)	25.0	1.4499	1.4530	+0.0031
36							1.4643	(5)	20.0	1.4666	1.4680	+0.0012
37							1.4532	(19)	25.0	1.4532	1.4524	−0.0008
								(20)	25.0	1.4532	1.4551	+0.0019
39							1.4515	(19)	25.0	1.4515	1.4528	+0.0013
40							1.4538	(23)	20.0	1.4560	1.4596	+0.0036
								(5)	20.0	1.4560	1.4610	+0.0050
								(20)	25.0	1.4538	1.4501	−0.0037
41							1.4542	(11)	25.0	1.4542	1.4537	−0.0005
42							1.4625	(19)	25.0	1.4625	1.4602	−0.0023
43							1.4611	(19)	25.0	1.4611	1.4598	−0.0013
44							1.4552	(19)	25.0	1.4552	1.4540	−0.0012
45							1.4596	(19)	25.0	1.4596	1.4616	+0.0020
46							1.4601	(19)	25.0	1.4601	1.4616	+0.0015

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(*Continued*)

Table V. Molar Refraction and *n-d* Intercept

Compd., No.	Lit. Ref.	$n^{25}D$[a] Obsd.	d_4^{25}[a] Obsd.	$R^{25}D$ Obsd.	$R^{25}D$ Est..	$\Delta R^{25}D$ Obsd. − Est.	*b* Obsd.	*b* Eq. 11	*b* Eq. 12	$n^{25}D$ Eq.13	$n^{25}D$ Eq. 14
1	TR	1.4569	1.0425	26.41	26.47	−0.06	0.9357	0.9334	0.9353	1.4546	1.4565
	(*11*)	1.4584	1.0429	26.48	26.47	+0.01	0.9370	0.9334	0.9353	1.4548	1.4567
2	TR	1.4520	1.0022	30.99	31.12	−0.13	0.9509	0.9517	0.9526	1.4528	1.4537
3	TR	1.4537	1.0081	30.91	31.12	−0.21	0.9497	0.9517	0.9526	1.4557	1.4566
	(*11*)	1.4590	1.0069	31.26	31.12	+0.14	0.9556	0.9517	0.9526	1.4551	1.4560
4	TR	1.4603	0.9841	35.97	35.79	+0.18	0.9683	0.9648	0.9650	1.4568	1.4570
	(*11*)	1.4572	0.9824	35.82	35.79	+0.03	0.9660	0.9648	0.9650	1.4560	1.4562
	(*19*)	1.4513	0.9883	35.21	35.79	−0.58	0.9571	0.9648	0.9650	1.4590	1.4592
5	TR	1.4568	0.9843	35.72	35.79	−0.07	0.9646	0.9648	0.9650	1.4570	1.4572
	(*11*)	1.4572	0.9833	35.79	35.79	0.00	0.9656	0.9648	0.9650	1.4564	1.4566
6	TR	1.4532	0.9785	35.68	35.77	−0.09	0.9640	0.9648	0.9650	1.4540	1.4542
	(*19*)	1.4521	0.9785	35.62	35.77	−0.15	0.9629	0.9648	0.9650	1.4540	1.4542
7	TR	1.4601	0.9641	40.69	40.42	+0.27	0.9781	0.9746	0.9745	1.4566	1.4565
8	TR	1.4550	0.9674	40.16	40.42	−0.26	0.9713	0.9746	0.9745	1.4583	1.4582
9	TR	1.4531	0.9613	40.27	40.45	−0.18	0.9725	0.9746	0.9745	1.4552	1.4551
	(*11*)	1.4580	0.9625	40.59	40.45	+0.14	0.9768	0.9746	0.9745	1.4558	1.4556
10	TR	1.4572	0.9618	40.56	40.45	+0.11	0.9763	0.9746	0.9745	1.4555	1.4553
11	TR	1.4579	0.9493	45.18	45.08	+0.10	0.9833	0.9822	0.9820	1.4568	1.4566
12	TR	1.4548	0.9495	44.90	45.08	−0.18	0.9800	0.9822	0.9820	1.4570	1.4568
13	TR	1.4589	0.9499	45.24	45.07	+0.17	0.9839	0.9822	0.9820	1.4572	1.4570
14	TR	1.4545	0.9455	45.07	45.07	0.00	0.9817	0.9822	0.9820	1.4550	1.4548
15	TR	1.4582	0.9494	45.20	45.11	+0.09	0.9835	0.9822	0.9820	1.4569	1.4567
	(*11*)	1.4593	0.9484	45.34	45.11	+0.23	0.9851	0.9822	0.9820	1.4564	1.4562
16	TR	1.4538	0.9339	49.64	49.69	−0.05	0.9868	0.9883	0.9880	1.4553	1.4550
17	TR	1.4564	0.9398	49.57	49.69	−0.12	0.9865	0.9883	0.9880	1.4582	1.4579
18	TR	1.4547	0.9344	49.70	49.73	−0.03	0.9875	0.9883	0.9880	1.4555	1.4552
19	TR	1.4510	0.9311	49.52	49.73	−0.21	0.9854	0.9883	0.9880	1.4539	1.4536
20	TR	1.4593	0.9380	49.94	49.73	+0.21	0.9903	0.9883	0.9880	1.4573	1.4570
21	TR	1.4559	0.9347	49.80	49.73	+0.07	0.9885	0.9883	0.9880	1.4557	1.4554
22	(*14*)	1.4227	1.1067	16.80	17.23	−0.43	0.8693	0.8602	0.8695	1.4136	1.4229
25	(*23*)	1.4508	1.0201	26.68	26.50	+0.18	0.9408	0.9334	0.9353	1.4434	1.4453
26	(*22*)	1.4349	1.0138	26.02	26.50	−0.48	0.9280	0.9334	0.9353	1.4403	1.4422
27	(*26*)	1.4686	1.0385	27.09	26.47	+0.62	0.9494	0.9334	0.9353	1.4526	1.4545
28	(*23*)	1.4527	0.9904	31.32	31.17	+0.15	0.9575	0.9517	0.9526	1.4469	1.4478
37	(*19*)	1.4524	0.9743	39.59	40.45	−0.86	0.9652	0.9746	0.9745	1.4618	1.4617
39	(*19*)	1.4528	0.9741	39.61	40.45	−0.84	0.9658	0.9746	0.9745	1.4616	1.4615
40	(*23*)	1.4574	0.9434	45.42	45.06	+0.36	0.9857	0.9822	0.9820	1.4539	1.4537
42	(*19*)	1.4602	0.9551	45.10	45.10	0.00	0.9826	0.9822	0.9820	1.4598	1.4596
43	(*19*)	1.4598	0.9427	49.73	49.76	−0.03	0.9884	0.9883	0.9880	1.4597	1.4594
44	(*19*)	1.4540	0.9236	54.32	54.34	−0.02	0.9922	0.9933	0.9929	1.4551	1.4547
45	(*19*)	1.4616	0.9343	54.47	54.41	+0.06	0.9944	0.9933	0.9929	1.4605	1.4601
46	(*19*)	1.4616	0.9273	59.04	59.06	−0.02	0.9979	0.9974	0.9970	1.4610	1.4606

[a] Observed values converted to 25° C.

Table VI. Abbe Number and Δn–Δd Relationships

Compd No.	$(\Delta d/\Delta t) \times 10^{-3}$ / $(\Delta n_D/\Delta t)^2$	$\Delta d/\Delta n_D$ Obsd.	$\Delta d/\Delta n_D$ Eq. 15	ν Obsd.	ν Eq. 16	ν Eq. 17
1	4.59	2.20	2.16	27.0	28.0	26.7
2	4.49	2.08	2.12	30.0	29.4	29.4
3	4.32	2.07	2.12	30.6	29.4	29.4
4	4.40	2.02	2.08	31.0	30.9	31.3
5	4.54	2.06	2.08	30.1	30.9	31.3
6	4.58	2.06	2.08	30.7	30.9	31.3
7	4.40	1.96	2.03	30.9	32.3	32.7
8	4.53	2.01	2.03	34.0	32.3	32.7
9	4.51	2.03	2.03	33.5	32.3	32.7
10	4.43	2.01	2.03	31.7	32.3	32.7
11	4.74	2.03	1.99	33.4	33.8	33.8
12	4.89	2.08	1.99	34.5	33.8	33.8
13	4.50	1.97	1.99	31.9	33.8	33.8
14	4.47	2.03	1.99	34.1	33.8	33.8
15	4.40	1.96	1.99	32.5	33.8	33.8
16	4.55	1.92	1.94	36.6	35.2	34.7
17	4.60	1.95	1.94	35.4	35.2	34.7
18	4.50	1.93	1.94	35.1	35.2	34.7
19	4.74	1.97	1.94	36.7	35.2	34.7
20	4.37	1.94	1.94	34.2	35.2	34.7
21	4.40	1.93	1.94	35.0	35.2	34.7
22	4.76	2.48	2.25	...	...	...

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