

Normal Boiling Points of 1, ω -Alkanedinitriles: The Highest Increment in a Homologous Series

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The normal boiling point for cyanogen is $-22\text{ }^{\circ}\text{C}$; for its next homologue, malononitrile, it is $219\text{ }^{\circ}\text{C}$. The difference of $241\text{ }^{\circ}\text{C}$ is apparently the highest one encountered for the addition of a single methylene group. Problems connected with boiling points and a rationalization for this observation are discussed in the context of intermolecular forces for liquids. A quantitative structure–property relationship (QSPR) study of the normal boiling points for monohaloalkanes and for the corresponding nitriles is reported. The behavior of the nitrile group as a pseudohalogen is also discussed. Normal boiling points of compounds having a cyano group bonded to an electron-attracting substituent situate the CN group close to being a pseudohalogen, but when the CN group is bonded to electron-donor substituents, the situation changes.

THE LIQUID STATE AND INTERMOLECULAR FORCES

Intermolecular forces range from the very weak ones such as those existing in liquefied noble gases to the strongest ones (hydrogen bonds) existing in hydrogen fluoride, in dimers of carboxylic acids (even in vapor state), or in liquids with multiple hydroxy groups such as glycols or water. The exceptional features of water (liquid state over a wide temperature range, expansion on freezing, high dielectric constant, and excellent solvent for a wide variety of substances) are responsible for making life possible on earth. Although ionic or metallic liquids also exist, they will not be discussed here because they are not molecular liquids. One should mention the important role of intermolecular forces and especially of hydrogen bonding in all life processes, in the transcription/translation processes involving DNA, in protein folding, receptor-agonist interactions, enzymatic mechanisms, etc.

Whereas intermolecular forces in crystals are compounded with conformational restrictions due to packing factors, liquids have molecular and conformational mobility (except for liquid crystals within certain limits). Liquids are more difficult to model than gases or solids. However, melting points of crystalline solids are also difficult to correlate with chemical structure due to packing factors, except for some classes of congeneric compounds.

Intermolecular forces are reflected by the following: vapor pressure versus temperature; boiling points at normal pressure (normal boiling points, NBPs); critical data; latent heat of vaporization versus temperature; viscosity; density and molar volume; optical properties such as the refractive index and molecular refractivity.

From all these clues, the easiest to measure with sufficient accuracy, and the most often cited for any compound, is the boiling point; usually, the NBP is cited, but seldom for

compounds that would boil at temperatures above $250\text{ }^{\circ}\text{C}$ at normal pressure because of decomposition. Many iodine derivatives decompose on heating even at lower temperatures because of the low C–I bond energy.

NITRILES AND THEIR NORMAL BOILING POINTS

The strongly electron-attracting nitrile (cyano) group is known to cause high dipole moments. For example, in the gas phase the dipole moments (in debye units) are as follows:¹

for Me–X		for Ph–X	
X = Cl	1.87 D	X = Cl	1.70 D
X = CF ₃	2.35 D	X = CF ₃	2.86 D
X = NO ₂	3.50 D	X = NO ₂	4.21 D
X = CN	3.94 D	X = CN	4.39 D

The resulting dipole–dipole interactions lead to strong molecular associations, manifested in higher NBPs, heats of vaporization, and viscosities than those of the corresponding hydrocarbons with comparable molecular weights.

Among thermodynamic properties, normal boiling points have been extensively investigated in quantitative structure–property relationships (QSPRs). From the molecular descriptors used in such correlations, topological indices have been among the most successful.^{2–6} For alkanes, such QSPR studies allow nowadays the prediction of NBPs within a range of 2 or 3 $^{\circ}\text{C}$.^{7–9} For various other classes of compounds many QSPR studies are available, and their accuracy range is often lower than 10 $^{\circ}\text{C}$.^{10–15}

Nitriles, however, proved to defy simple approaches. Thus, a recent study by Wessel and Jurs for a diverse set of industrially important chemicals containing nitrogen with mean-square-root errors of about 9 $^{\circ}\text{C}$ led to satisfactory results for mononitriles but to very large errors for two dinitriles, namely, cyanogen and malononitrile.¹² We have therefore decided to look more closely into this matter. A comprehensive review on malononitrile is available.¹⁶

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Table 1. Cyano Group as a Pseudohalogen: NBP for X–Y or X₂ Compounds^a

(pseudo)- halogen X	FW	X–CN		X–X	
		NBP (°C)	FW	NBP (°C)	FW
F	19	–72	49	–188	38
CN	26	–22	60	–22	60
Cl	35	13	66	–35	71
Br	80	62	110	56	160
I	127	184	157	178	254

^a Figures have been rounded off to the nearest integer.**Table 2.** NBPs of Cyanotrihalomethanes Hal₃C–CN and of Tetrahalomethanes Hal₃C–X (Hal = F, Cl, Br)^a

X	F		Cl		Br	
	NBP (°C)	FW	NBP (°C)	FW	NBP (°C)	FW
F	–128	88	25	137	107	271
Cl	–82	104	77	154	160	287
CN	–62	95	84	149	170	278
Br	–79	149	104	198	190	332
I	–23	196	141	245		

^a Figures have been rounded off to the nearest integer.

CYANO GROUP AS A PSEUDOHALOGEN

Groups such as cyano, thiocyno, cyanato, and azido are considered to be pseudohalogens.^{17–19} In this paper we shall focus only on the cyano group. There are also significant differences, however, between some compounds of halogens and pseudohalogens, for instance the fact that hydrogen cyanide is a much weaker acid (with $pK_a = 9.2$) than hydrogen halides. Also, the coordinating ability of the cyanide anion for iron leads to a high toxicity, whereas each of the halide anions has a different biological significance. One should also recall that the cyano group is bidentate, being able to form covalent or coordinative bonds at the carbon or nitrogen atoms. Thus, the elongated shape of the cyano group makes it different from the spherical halogens.

It is known that molecular weights have a large influence on NBPs. According to its formula weight (FW), a CN group is intermediate between a fluorine and a chlorine atom. On comparing NBPs^{20–22} of simple halogens, interhalogens, cyanogen, or cyanogen halide linear molecules (Table 1), it can be seen that the cyano group does indeed behave as a pseudohalogen. On considering cyanogen halides, the CN group is placed by NBPs between fluorine and chlorine. However, on comparing NBPs of cyanogen and those of elemental halogens, the CN group is situated between chlorine and bromine, as if the CN group had a slightly higher formula weight.

In Table 2 the NBPs of cyanotrihalomethanes, X₃C–CN, and of tetrahalomethanes, CX₄, are shown. It can be seen that the cyano group behaves again as a pseudohalogen situated between chlorine and bromine.

Although some physical data support the idea that the CN group manifests itself as a pseudohalogen, its chemical behavior in organic compounds is quite different from that of halogens. The C–Cl, C–Br, and C–I bond strengths are much lower than the bond strength of the C–CN bond; therefore, these halogens (unlike CN groups) are good leaving groups. In the next section we shall examine organic compounds whose NBPs are much higher than those of the corresponding halogen compounds, so that the cyano group

would be situated beyond iodine; in such cases, the notion of pseudohalogen is no longer justified.

NORMAL BOILING POINTS OF NITRILES AND DINITRILES

Mononitriles have NBPs which are quite high when compared with the corresponding halides (Table 3). In Table 3 structures of halogen derivatives are indicated (in abbreviated form) according to IUPAC nomenclature rules; for nitriles, however, to achieve consistency, the CN group is considered as a pseudohalogen; therefore, the nomenclature is no longer according to IUPAC. In these cases a CN group increases the NBP much more than the heaviest stable halogen atom, namely, iodine. An analogous behavior is apparent when comparing halocarbonyl or cyanocarbonyl compounds (Table 4). Also, the NBPs of 1, ω -alkanedihalides for linear alkane chains with one through four carbon atoms, X(CH₂)_nX (with $n = 1–4$) are much lower than for the corresponding 1, ω -alkanedinitriles (Table 5).

As seen from Table 6 for *gem*-dihalides or *gem*-dinitriles of methane, ethane, or propane, a similar trend with higher NBPs for X = CN than for X = Hal is observed; moreover, one sees the curious trend that when the X group in R–X is I or CN, the NBPs decrease progressively in the above series with increasing molecular weight, whereas the corresponding compounds with X = F, Cl, or Br exhibit the reverse, normal behavior. A break in Table 6 separates the compounds with normal and abnormal behavior.

QSPR STUDY OF MONOHALO DERIVATIVES AND OF THEIR CYANO ANALOGUES

For correlating the chemical structure with the NBP for the data presented in Table 3 we selected eleven topological indices: the information indices IC₁–IC₃ and CIC₁–CIC₃;²³ the Wiener index *W*; the valence connectivity indices ⁰ χ^v –² χ^v ; ^{4,24} and the average distance-sum connectivity adapted for heteroatoms based on their electronegativities (Balaban's index, *J_x*).^{25,26} All indices except the last one were computed using the program POLLY.²⁷

Due to the fact that the scale of the various topological indices may differ by several orders of magnitude, all indices were transformed by first adding 1 to the index and then taking the natural logarithm of this result. The transformed version of the indices was used in all analyses. The CORR procedure of the SAS statistical package³² was used to identify intercorrelated indices. The elimination of such indices reduced to four the number of selected TIs, namely, IC₂, CIC₂, ¹ χ^v , and *J_x*.

An all-subset regression was accomplished using the REG procedure of the same statistical package,³² which indicated that ¹ χ^v and *J_x* gave the best results; IC₂ and CIC₂ gave the next best results. The drawback of IC and CIC indices is that the nature of the halogen does not affect the value of these indices.

Experimental and calculated data for NBPs of monohalo derivatives with one through five carbon atoms and the corresponding mononitriles with two to six carbon atoms are presented in Table 3, above the solid line. Some nitriles with six to eight carbon atoms are also included below the solid line, but they have no halogen counterparts, and the correlations discussed below do not include them.

Table 3. NBPs ($^{\circ}\text{C}$) of Organic Halides and Nitriles R-X and QSAR in Terms of $^1\chi^v$ and J_x

compd	NBP _{exp} ^a	NBP _{calc} ^a	diff _{exp-calc} ^a	$^1\chi^v$ ^b	J_x ^b
Me-F	-78	-81	3	0.3206	0.6054
Et-F	-38	-32	-6	0.6801	0.9143
Pr-F	3	3	0	0.9058	1.0550
Bu-F	33	34	-1	1.0899	1.1346
sBu-F	25	22	3	1.0685	1.2334
1-C ₅ -F	63	62	1	1.2453	1.1860
Me-Cl	-24	-23	-1	0.7580	0.6152
Et-Cl	12	10	2	0.9199	0.9207
Pr-Cl	47	47	0	1.1016	1.0588
iPr-Cl	36	34	2	1.0328	1.1656
Bu-Cl	79	79	0	1.2553	1.1375
sBu-Cl	68	69	-1	1.2081	1.2369
iBu-Cl	69	70	-1	1.2134	1.2407
tBu-Cl	51	51	0	1.1207	1.3635
1-Cl-C ₅	108	106	2	1.3885	1.1881
2-Cl-C ₅	97	97	0	1.3473	1.2672
2-Me-1-Cl-C ₄	100	100	0	1.3617	1.3043
3-Me-1-Cl-C ₄	99	98	1	1.3520	1.2709
CEt ₂ -Cl	98	99	-1	1.3571	1.2999
Me-Br	4	10	-6	1.0865	0.6403
Et-Br	39	33	6	1.1301	0.9357
Pr-Br	71	69	2	1.2798	1.0685
iPr-Br	60	56	4	1.1906	1.1768
Bu-Br	102	99	3	1.4100	1.1445
sBu-Br	91	90	1	1.3421	1.2453
iBu-Br	91	97	-6	1.3742	1.2479
tBu-Br	73	77	-4	1.2476	1.3727
1-Br-C ₅	130	125	5	1.5252	1.1936
2-Br-C ₅	117	116	1	1.4649	1.2737
2-Me-Br-1-C ₄	121	125	-4	1.5019	1.3100
3-Me-1-Br-C ₄	120	122	-2	1.4934	1.2765
CEt ₂ -Br	119	119	0	1.4736	1.3070
Me-I	43	51	-8	1.2627	0.6689
Et-I	73	66	7	1.2528	0.9532
Pr-I	103	100	3	1.3863	1.0801
iPr-I	90	87	3	1.2862	1.1900
Bu-I	131	127	4	1.5041	1.1531
sBu-I	120	117	3	1.4248	1.2553
iBu-I	121	127	-6	1.4716	1.2568
tBu-I	100	106	-6	1.3265	1.3833
1-I-C ₅	155	150	5	1.6094	1.2000
2-I-C ₅	141	141	0	1.5384	1.2818
2-Me-1-I-C ₄	148	153	-5	1.5880	1.3169
3-Me-1-I-C ₄	147	149	-2	1.5802	1.2829
CEt ₂ -I	146	145	1	1.5465	1.3156
Me-CN	82	71	11	0.5446	1.2196
Et-CN	97	104	-7	0.8259	1.2173
Pr-CN	118	126	-8	1.0239	1.2366
iPr-CN	104	109	-5	0.9810	1.3592
Bu-CN	141	143	-2	1.1891	1.2565
sBu-CN	125	128	-3	1.1647	1.3880
iBu-CN	131	129	2	1.1442	1.3483
tBu-CN	106	108	-2	1.0899	1.5065
1-CN-C ₅	164	158	6	1.3308	1.2737
2-CN-C ₅	146	145	1	1.3097	1.3888
2-Me-1-CN-C ₄	154	147	7	1.2920	1.3431
3-Me-1-CN-C ₄	157	158	-1	1.3308	1.2737
CEt ₂ -CN	146	142	4	1.3199	1.4339
EtCMe ₂ -CN	129	126	3	1.2624	1.5304
1-CN-C ₆	183	171	12	1.4549	1.2881
2-CN-C ₆	164	160	4	1.4363	1.3840
3-Me-1-CN-C ₅	172	158	14	1.4298	1.3992
4-Me-1-CN-C ₅	180	159	21	1.4298	1.3830
5-Me-1-CN-C ₅	180	158	22	1.3308	1.2737
1-CN-C ₇	199	183	16	1.5653	1.3002

^a Figures have been rounded off to the nearest integer. ^b Topological indices $^1\chi^v$ and J_x are expressed by converting their values (y) into $\ln(1 + y)$.

Table 4. NBPs of Halocarbonyl Derivatives (Iodine Derivatives Are Not Available)^a

X	NBP ($^{\circ}\text{C}$)	
	EtOCOX	ClCOX
F	57	-45
Cl	95	8
Br	116	25
CN	116	128

^a Figures have been rounded off to the nearest integer.

Table 5. NBPs of 1, ω -Dihalides and 1, ω -Biscyanides of Linear Alkanes C₁-C₄^a

X	NBP ($^{\circ}\text{C}$)			
	XCH ₂ X	X(CH ₂) ₂ X	X(CH ₂) ₃ X	X(CH ₂) ₄ X
F	-52	31	42	78
Cl	40	84	121	154
Br	97	131	167	197
I	181	200	227	
CN	219	266	286	295

^a Figures have been rounded off to the nearest integer.

Table 6. NBPs of *gem*-Bis(pseudo)halides of Alkanes C₁-C₃^a

X	NBP ($^{\circ}\text{C}$)		
	CH ₂ X ₂	MeCHX ₂	Me ₂ CX ₂
F	-52	-25	0
Cl	40	58	71
Br	97	113	115
I	181	178	148
CN	219	198	170

^a Figures have been rounded off to the nearest integer.

A comment on how the $^1\chi^v$ and J_x indices vary with increasing size and branching of molecules needs to be added. Both these indices increase with increasing size. The nature of the halogen X in R-X molecules with the same R group also leads to a progressive increase in the series F, Cl, Br, and I; this increase is steep for $^1\chi^v$ but moderate for J_x . However, increasing branching of the R group for isomeric molecules leads to decreasing values for $^1\chi^v$ but to increasing values for J_x . Of course, as a general rule, experimental NBPs increase with increasing size and molecular weight of molecules and decrease with molecular branching; only poly(fluoroalkanes) are exceptions to this rule, as mentioned earlier.¹³

The corresponding equations are shown in Table 7a,b with the statistical parameters. For the chloro derivatives J_x was not a significant parameter, so that a monoparametric equation in terms of $^1\chi^v$ gave in this case satisfactory results. For all other compounds from Table 3, such monoparametric equations led to worse results than those presented in both parts a and b of Table 7. Intercorrelation factors between the four selected indices are presented in Table 8; one can see that no significant intercorrelation is present. It can be observed from Tables 3 and 7a that the correlation for nitriles is slightly poorer than for the halogens; however, the agreement between the experimental and calculated NBPs is quite good. Remarkably, the coefficients of the $^1\chi^v$ parameter are similar for Br and I in Table 7a and for all halogens in Table 7b; this fact is reminiscent of the observation presented in the earlier paper¹³ about the fact

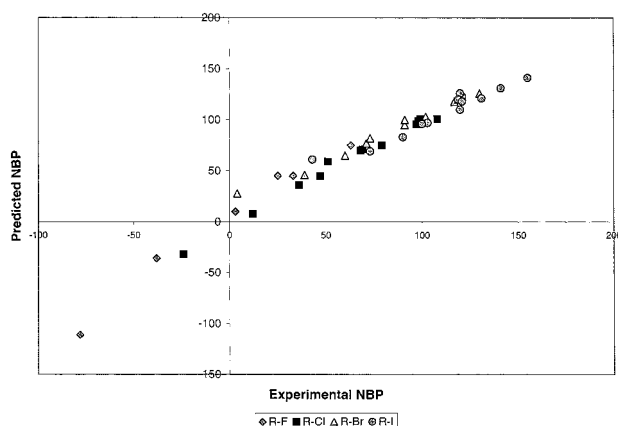
Table 7. Correlation Equations for NBP and Statistical Parameters

(a) In Terms of $^1\chi^v$ and J_x					
	NBP	s	r	F	
RF	$(208 \pm 23)^1\chi^v - (84.0 \pm 32)J_x - (96.8 \pm 15)$	4.3	0.998	355	
RCI	$(204 \pm 2)^1\chi^v - (177 \pm 2)$	1.4	0.999	9444	
RBr	$(203 \pm 12)^1\chi^v + (45.6 \pm 9.3)J_x - (239 \pm 12)$	4.5	0.994	404	
RI	$(195 \pm 15)^1\chi^v + (59.3 \pm 10)J_x - (235 \pm 17)$	5.3	0.989	235	
RCN	$(117 \pm 8.4)^1\chi^v - (92.5 \pm 22)J_x + (120 \pm 27)$	6.1	0.976	99	
(b) In Terms of IC_2 and CIC_2					
	NBP	s	r	F	
RF	$(223 \pm 27)IC_2 + (197 \pm 47)CIC_2 - (406 \pm 38)$	10.2	0.988	62	
RCI	$(230 \pm 16)IC_2 + (146 \pm 16)CIC_2 - (333 \pm 27)$	9.0	0.978	109	
RBr	$(218 \pm 16)IC_2 + (135 \pm 16)CIC_2 - (286 \pm 27)$	8.7	0.977	104	
RI	$(198 \pm 15)IC_2 + (115 \pm 15)CIC_2 - (217 \pm 25)$	8.4	0.974	92	
RCN	$(176 \pm 30)IC_2 + (93.9 \pm 20)CIC_2 - (168 \pm 42)$	11.4	0.914	25	

Table 8. Intercorrelation Matrix for the Four Selected TIs^a

	$^1\chi^v$	J_x	IC_2	CIC_2
$^1\chi^v$	1.000	0.702	0.802	0.178
J_x		1.000	0.451	0.655
IC_2			1.000	-0.331
CIC_2				1.000

^a Topological indices $^1\chi^v$ and J_x are shown by converting their values (y) into $\ln(1 + y)$.

**Figure 1.** Plot of the predicted NBP versus the experimental NBP for the combined set of 45 monohaloalkanes from Table 3 in terms of two TIs, namely, $^1\chi^v$ and J_x .

that one might consider a “generalized halogen” with a stepwise increment for the four halogens F, Cl, Br, and I. Though the aim of the present paper was to discuss nitriles and not haloderivatives (the NBPs of these last compounds were the object of a QSPR study in the earlier paper¹³), one can use the same parameters as in Table 7a for a correlation of NBPs for all 45 halogen derivatives presented in Table 3 according to the following equation:

$$NBP = (180 \pm 7.8)^1\chi^v + (34 \pm 10)J_x - (189 \pm 9.2)$$

$$s = 10\text{ }^\circ\text{C} \quad r = 0.9823 \quad F = 579$$

The diagram shown for this correlation in Figure 1 indicates that only 2-butyl fluoride and three halomethanes with F, Br, and I have deviations above 14 °C between observed and predicted NBPs.

Interestingly, the last equation of Table 7a works even for other aliphatic mononitriles with six to eight carbon atoms, presented at the bottom of Table 3 below the full

Table 9. NBPs (°C) of Unsaturated Nitriles and QSAR in Terms of IC_2 and CIC_2

nitrile	IC_2	CIC_2	NBP _{exp}	NBP _{calc}	diff _{exp-calc}
C=CC#N	1.2590	0.2515	78	80	-2
C#CC#N	1.2006	0.0000	43	40	3
C=CCC#N	1.3666	0.3365	119	112	7
CC=CC#N	1.2936	0.5158	113	116	-3
CC(=C)C#N	1.2936	0.5158	91	116	-25
CC=C(C)C#N	1.2548	0.7853	138	137	1
CC(C)=CC#N	1.2102	0.8531	141	135	6
C=CCCC#N	1.3689	0.5704	140	138	2
CCC=CC#N	1.3930	0.5146	136	137	-1
C=CC=CC#N	1.3468	0.4787	137	123	14
CCC(C)=CC#N	1.3625	0.7391	142	155	-13
CC(C)C=CC#N	1.3300	0.7971	155	155	0
CC(C)=CCC#N	1.3300	0.7971	166	155	11

line; however, in these cases, all calculated values are lower than the experimental ones.

Unsaturation in the nitrile chain lowers appreciably the NBP, as seen in Table 8. Using the same descriptors as in Table 7b for these nitriles with three to six carbon atoms having one or two double bonds or one triple bond (denoted by # in Table 9 which uses Smiles notation for structures), the QSAR results presented in Table 9 were obtained with the following equation:

$$NBP = (214 \pm 52)IC_2 + (109 \pm 13)CIC_2 - (217 \pm 67)$$

$$s = 11\text{ }^\circ\text{C} \quad r = 0.9121 \quad F = 52$$

A GUESSING GAME

On addressing an audience of chemists, the following guessing game was proposed: the audience was given the NBPs of the 1,ω-alkanedinitriles $X(CH_2)_nX$ with $n = 1-4$, namely, malononitrile, succinonitrile, adiponitrile, and capronitrile (i.e., the last line in Table 5). Then everyone was asked to guess the NBP temperature interval for oxalonitrile (the compound with $n = 0$) by putting a mark in one of the following eight intervals: <-20 ; -20 to $+20$; $+20$ to $+60$; $+60$ to $+100$; $+100$ to $+140$; $+140$ to $+180$; $+180$ to $+220$; and $>+220$ °C. Remarkably, no member of the audience guessed that oxalonitrile (cyanogen with NBP = -22 °C) should appear in the first temperature interval (NBP ≤ -20 °C). The other seven temperature intervals were about equally populated with marks.

LARGEST INCREMENT IN NBP FOR A HOMOLOGOUS SERIES

The two compounds (cyanogen and manonitrile) mentioned to be outliers in the QSPR study cited earlier¹² represent the pair with the largest NBP increment on adding one methylene group, as seen from Table 10. In this table, one compares the next two homologues having various simple groups bonded either directly (R_2) or via a methylene group (RCH_2R), where R can be a halogen, a cyano group, an alkyl, an alkoxy, or an organic electronegative group. Breaks in the table delineate various related classes of compounds.

The first entry of the above two compounds constitutes a class by itself. The huge difference of 241 °C between the NBPs of cyanogen (oxalonitrile, with NBP = -22 °C) and malononitrile (with NBP = 219 °C) can be explained by the fact that cyanogen has a linear geometry and hence a

Table 10. Differences in NBPs for Compounds Differing by One Methylene Group^a

R	NBP (°C)		
	R ₂	RCH ₂ R	diff
CN	-22	219	241
H	-253	-162	91
CF ₃	-78	1	79
CH ₃ -CO	88	138	50
CH ₃	-89	-42	47
HC≡C	10	55	45
F	-188	-52	136
Cl	-35	40	75
Br	56	97	41
I	184	182	-2
Et	0	37	37
MeO	14	42	28
EtO	63	88	25
MeS	110	149	39
EtS	154	181	27
CCl ₃	186	206	20
COOMe	163	181	18
COOEt	185	199	14
COOPr	211	229	18
COOBu	242	256	14
Ph	256	264	12

^a Figures have been rounded off to the nearest integer.

zero dipole moment, whereas malononitrile is a V-shaped molecule with a high dipole moment, 3.58 D.^{28,29} The calculated polarizability of malononitrile is abnormally high in comparison with calculated values.^{30,31}

A few other comments in Table 10 should be added. The first nine entries show differences in NBPs that are higher than 40 °C for the two homologues. Among these, the first six have electronegative or slightly electron-donating groups; the next class includes the four stable halogens, and the trend in this group with progressively decreasing electronegativity is quite interesting, starting with the next highest NBP difference in the whole table (for fluorine) and ending with a negative difference (for iodine). All these entries have linear R₂ and bent R₂CH₂ molecules for the two homologues, respectively.

The last class with NBP differences lower than 40 °C, however, demonstrates that electronegativity by itself does not provide a full explanation for the data contained in Table 10. Indeed, here again we encounter groups with electron-donating as well as with electron-accepting properties. However, in this class the R₂ molecules have no longer linear geometries except for biphenyl and hexachloroethane.

OTHER DINITRILES

A comparison between volatilities of dinitriles of four-carbon dicarboxylic acids is interesting, despite the incompletely matched data. Succinonitrile has a NBP of 266 °C and a dipole moment of 3.93 D. From the two stereoisomeric olefinic congeners, the dinitrile of fumaric acid with *E*-geometry is more volatile (NBP of 186 °C, subliming even under 100 °C) than the dinitrile of maleic acid (with a higher dipole moment because of its *Z*-geometry) which has a BP of 111 °C at 20 Torr and 99 °C at 13 Torr. The alkynic congener which has a linear geometry and zero dipole moment (dicyanoacetylene or acetylenedicarbonitrile, C₄N₂)

has a NBP of only 77 °C and sublimates easily. Interestingly, the dinitrile C₆N₂ of hexadiynedioic acid with two triple bonds (with linear geometry) has a NBP of only 154 °C.

Isomers of benzodinitrile also have volatilities that attest the importance of dipole moments: phthalonitrile with the highest dipole moment has at 10 Torr a boiling point of 151 °C; isophthalonitrile with a dipole moment which is about half as large has the BP of 140 °C at the same reduced pressure; and terephthalonitrile with a zero dipole moment sublimates at normal pressure at temperatures starting at 153 °C.

When the CN group is attached to an electron-acceptor substituent, the polarity of the bond is low and the NBP is within the range expected for a pseudohalogen with a formula weight close to that of chlorine. However, when the CN group is bonded to an electron-donor substituent, the high polarity of the resulting bond enhances appreciably the NBP. The conclusion is that NBPs are the result of a multiplicity of factors inherent in determining the intermolecular forces that exist in the liquid state. In certain cases such as the two homologous dinitriles with two and three carbon atoms, QSPR studies should not ignore differences between these intermolecular interactions.

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