FORECASTING THE CRITICAL TEMPERATURE FOR A HYDROCARBON FROM THE STRUCTURAL FORMULA

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A simple method is proposed for predicting the critical temperature of a hydrocarbon with an accuracy of about 3 K from the structural formula alone.

Methods have been devised [1-4] for predicting the properties of normal (unassociated) substances from the structural formulas, part of which involves calculating the critical temperature T_c and critical molar volume V_c. In [2], a formula was derived relating T_c to the dispersion constant, which is capable of being calculated by summing constant atomic increments [2, 4]. The mean error in T_c for hydrocarbons in that method is 2.5% (13 K), i.e., is of the same order as the differences between the T_c for isomers. Here I examine what structure features have the main effect on T_c and propose a method more accurate than that of [2] for predicting it. A similar treatment for the critical volume has been given in [3].

T_c for a hydrocarbon C_nH_m is

$$T_c = T_c^{(0)}(n) + \Sigma \Delta T_c^{(i)} n_i. \tag{1}$$

Here $T_c^{(0)}(n)$ is that temperature for the n-alkane C_nH_{2n+2}; $\Delta T_c^{(i)}$ are corrections for structural features, and n_i is the number of type i elements in the molecule (i = 1, 2, ..., 6). I list below the structural elements that correspond to the corrections.

1. Nonterminal branching gives $\Delta T_c^{(1)} = -5$ K. Here and subsequently, branching means single branching in the carbon chain, i.e., a $-\overset{|}{\underset{|}{C}}H$ group or a $=\overset{|}{C}-$ one for alkenes and aromatic hydrocarbons. A $-\overset{|}{\underset{|}{C}}-$ group is considered as two branches, e.g., for an alkane molecule containing $n_1^{(1)}$ C atoms of $-\overset{|}{\underset{|}{C}}H$ type and $n_1^{(2)}$ ones of $-\overset{|}{\underset{|}{C}}-$, type, where $n_1 = n_1^{(1)} + 2n_1^{(2)}$. Correction 1 relates only to branching not forming part of the terminal $-CH(CH_3)_2$, $-C(CH_3)_3$, $=C(CH_3)_2$, etc., groups. The latter structures are incorporated in the next point.

2. Terminal branching gives $\Delta T_c^{(2)} = -10$ K, which applies for all situations where the C atom is joined directly to two or three terminal C atoms. Correspondingly, in the first case we have one terminal branch and two in the second. For example, a terminal $-CH(CH_3)_2$ group in alkane gives $n_2 = 1$, while a $-C(CH_3)_3$ group gives $n_2 = 2$.

3. A double bond that is not a terminal one gives $\Delta T_c^{(3)} = +5$ K; $n_3 = 3$ for a benzene ring.

4. A terminal double bond, i.e., a $=CH_2$ group in an alkene, gives $\Delta T_c^{(4)} = -5$ K.

5. A ring gives $\Delta T_c^{(5)} = +40$ K, which is the same for all saturated and unsaturated rings ranging from three-membered to six-membered inclusive.

6. A series of branches in sequence, i.e., where the branches are separated by single C–C bonds, gives $\Delta T_c^{(6)} = +10$ K.

It is easy to calculate n_i, and for clarity, we use a schematic representation of the carbon skeleton in which the C atoms are denoted by filled circles and the C–C bonds by lines

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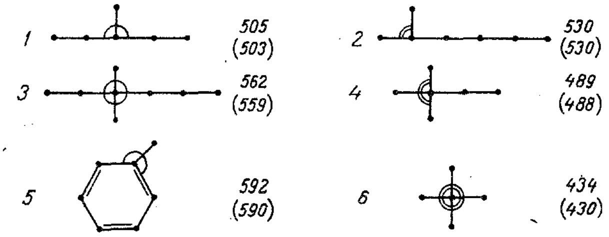

Fig. 1

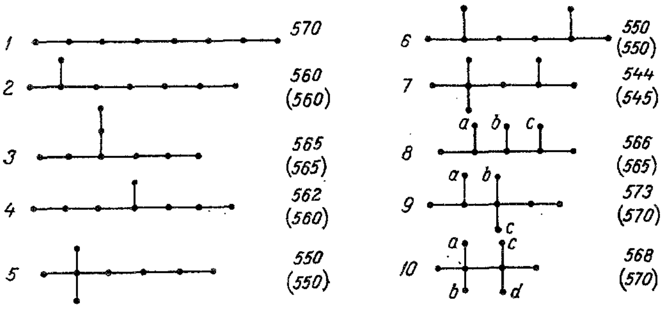

Fig. 2

Fig. 1. Examples of counting corrections 1 and 2. The double arcs denote terminal bond angles, number n_2, while the single arcs denote angles not relating to terminal branches, number $2 \cdot n_1$: 1) 3-methylpentane, $n_1 = 1$, $n_2 = 0$; 2) 1-methylhexane, $n_1 = 0$, $n_2 = 1$; 3) 3,3-dimethylhexane, $n_1 = 2$, $n_2 = 0$; 4) 2,2-dimethylbutane, $n_1 = 0$, $n_2 = 2$; 5) methylbenzene, $n_1 = 1$, $n_2 = 0$; 6) neopentane, $n_1 = 0$, $n_2 = 4$; the numbers by the substances are the measured T_c, while those in parentheses are ones calculated from (1).

Fig. 2. Some octane isomers: 1) n-octane; 2-4) isomers with slight branching; 5-7) isomers with minimal T_c; 8-10) isomers where correction 6 is required (see explanation in text).

(Figs. 1 and 2). To derive n_1 and n_2, we distinguish also the angles between C—C bonds whose vertices are involved in branching. Then n_2 is equal to the number of bond angles joining the terminal C atoms, while n_1 is half the bond angles relating to the other branchings. An interesting example is provided by neopentane, for which $n_1 = 0$ and $n_2 = 4$.

It is not difficult to incorporate corrections 3-5, since the result for an aromatic ring is not dependent on how the three double bonds are distributed in accordance with the Kekule formula. The complete correction for an aromatic ring is $\Delta T_c^{(ar)} = \Delta T_c^{(5)} + 3\Delta T_c^{(3)} = 55$ K.

Correction 6 is very important. The positive sign reflects the nonmonotone dependence of T_c on the degree of carbon skeleton branching. The T_c for hydrocarbons are reduced relative to $T_c^{(0)}$ if there are a few branches, while when the branches become more numerous, T_c at first increases again up to the initial $T_c^{(0)}$. Figure 2 illustrates this for octane isomers. Correction 6 is important. Substance 8 (2,3,4-trimethylpentane) has two pairs of adjacent branches *a*b and bc, for which $n_6 = 2$. In substance 9 (2,3,3-trimethylpentane), simple branching coexists with double. As double branching is considered as two simple cases, we have here two pairs of adjacent branches *a*b and ac, and $n_6 = 2$, as previously. Similarly, for substance 10 (2,2,3,3-tetramethylbutane), there are four pairs of adjacent branches *a*c, *a*d, bc, and bd, so $n_6 = 4$.

Table 1 gives additional examples. The figures there and in the illustrations indicate a very good accuracy for (1), particularly for saturated hydrocarbons. For the C_4 to C_8 alkanes, the average error is only 1.5 K (0.3%). The errors increase for nonane isomers, and the mean error for all alkanes is 3 K. The same mean error is obtained for the alkenes and the cyclic hydrocarbons (the check set included 117 substances: all hydrocarbons for which measured T_c are available). The errors in (1) are much less than in all other ways of pre-

TABLE 1. Applications of (1)

Substance	n	n_1	n_2	n_3	n_4	n_5	n_6	$T_C^{(0)}$, K	T_C, K	
									(1)	exp
3-methylhexane	7	1	0	0	0	0	0	540	535	535
2-methylhexane	7	0	1	0	0	0	0	540	530	530
2,2-dimethylpentane	7	0	2	0	0	0	0	540	520	520
2,3-dimethylpentane	7	1	1	0	0	0	1	540	535	537
2,2,3-trimethylbutane	7	0	3	0	0	0	2	540	530	531
2,2,3,3-tetramethylbutane	8	0	4	0	0	0	4	570	570	568
2,4,4-trimethylpent-2-ene	8	0	3	1	0	0	0	570	545	543
n-hex-1-ene	6	0	0	0	1	0	0	570	505	504
cyclopentane	5	0	0	0	0	1	0	470	510	512
ethylbenzene	8	1	0	3	0	1	0	570	620	617
1-methyl-2-ethylbenzene	9	2	0	3	0	1	1	595	650	653

dicting T_C for hydrocarbons. For example, the Forman-Thodos method [5] gives a mean error of 7.3 K for the same set [6] in spite of the enormous number (about 150!) of empirical constants. The Mathur–Kuloor method [7], which does not incorporate structural isomerism at all, gives errors about 3-4 times ours.

Results similar in accuracy ($\langle \delta T_C \rangle = 0.6\%$) have been given by Stiel and Thodos [8] in predicting alkane critical temperatures, where a formula was given relating $T_C - T_C^{(0)}$ to characteristics of the carbon skeleton: the Wiener number W and the Platt number Pl. Generally, the correlation between alkane properties on the one hand and W and Pl on the other is frequently used [9, 10], although it has two marked disadvantages. Firstly, the approach cannot be extended to other hydrocarbon classes and is restricted to alkanes. Secondly, it is complicated to calculate W and Pl, which makes the entire method cumbersome and excessively formal. Our combination of simplicity and accuracy is based mainly on an informal consideration of the entire data set for hydrocarbon critical temperatures, where no a priori forms are specified.

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