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Peculiar Features of Intermolecular Interactions in Organic Compounds with Anomalously Low Boiling Points

G. V. Korolev, A. A. Il'in, M. M. Mogilevich, R. V. Chebunin, and M. E. Solov'ev

Institute of Problems of Chemical Physics, Russian Academy of Sciences, Chernogolovka, Russia
Yaroslavl State Technical University, Yaroslavl, Russia
Institute of Solution Chemistry, Russian Academy of Sciences, Ivanovo, Russia

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Abstract—Comparison of the boiling points (T_b) of the members of the organic triglyceride and anhydride homologous series (with unbranched hydrocarbon chains) with the T_b of *n*-alkanes at equal Van der Waals molecular volumes showed that the boiling points of compounds with functional groups, centers of strong intermolecular interactions, are lower than those of hydrocarbons, compounds containing no functional groups. In the triglyceride and anhydride homologous series, the T_b sharply (by more than 100°C) decreases from homolog to homolog (rather than increasing, as usually observed). To explain these anomalies, computer modeling of conformations of individual and associated molecules was performed. Standard enthalpies of vaporization (ΔH_v^0), energies of intermolecular interactions (E_{IMI}), and the ratios $E_{IMI}/\Delta H_v^0 = \alpha_{IMI}$ (coefficients of intermolecular interactions, which may serve as a criterion of the fraction of such interactions, converted into intramolecular interactions) were calculated for all the compounds. The T_b of triglycerides and anhydrides calculated in terms of the model of pair reversible interactions of like atomic groups with allowance for α_{IMI} nicely fit with experimental values. The resulting data show that part of intermolecular interactions in triglycerides and anhydrides converts into intramolecular, which results in anomalously low T_b and sharp fall of T_b along the triglyceride and anhydride homologous series.

Computer-aided analysis of the boiling points (T_b) of more than 5000 organic compounds showed that these values are mostly affected by intermolecular interactions and molecular shape (conformational state) [1, 2]. The boiling points of organic compounds of different classes but with the same shape and Van der Waals molecular volume (V_W) increase in parallel with the energy of intermolecular interactions of corresponding functional groups. However, carboxylic triglycerides and anhydrides, which possess centers of potentially strong intermolecular interactions (COO and OCOCO) groups, have lower T_b than *n*-alkanes with the same V_W values but possessing centers of weak intermolecular interactions (CH_2 and CH_3). This anomaly was explained in terms of compacting molecules the of higher triglycerides and anhydrides at the boiling point, with simultaneous conversion of intermolecular bonds into intramolecular [2].

In the present work we checked the validity of this assumption by computer modeling of associative structures in the triglyceride and anhydride homologous series, as well as by estimating the fraction of intermolecular (associative) bonds converted into intramolecular.

Procedure of computer analysis. Computer modeling was performed using the Cambrige Soft Chem Office 3D program package (Ver. 5.0). Termodynamically most favorable conformers were determined by calculation of the molecular geometry at minimium total energy. The equilibrium conformations of individual and associated molecules were determined by molecular mechanics calculations [3, 4]. The energies of intermolecular interactions were found by calculating the structures of associates of 16 or 32 molecules at minimum total energies. The total energy of an associate and the energy of intermolecular interactions per one molecule (E_{IMI}) were calculated by the procedure in [4]. Minimization of the total energy of individual molecules or associates was performed by randomization. The total energy minimum was searched for 10–20 randomly chosen configurations, each with its specific minimal energy. Thus a set of minimal total energies of molecules (associates) was formed, corresponding to the most stable conformers, and then the conformer with a minimal total energy was chosen from the whole set of conformers.

The most thermodynamically favorable associative

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structures and conformations of individual molecules of triglycerides and anhydrides of unbranched carboxylic acids from acetic to stearic were determined. The T_b values of triglycerides, anhydrides, and alkanes (the latter were used for comparison purposes as compounds containing no functional groups) were taken from the data base comprising the most reliable reference T_b values of organic compounds [5–7]. The Van der Wals molecular volumes (V_W) were calculated from the atomic radii and interatomic distances by the procedure in [8, 9].

Results and discussion. Let us first consider in more detail the trends in T_b along the triglyceride, anhydride, and *n*-alkane series on the basis of the $T_b = f(V_W)$ curves (Fig. 1) whose comparison is correct at V_W = const. Van der Waals molecular volumes are a characteristic parameter of molecular size, and we can accept, as a first approximation, as it has been done in [2], that the contribution of weak (dispersion) intermolecular interactions of CH_2 groups into the intensity of intermolecular interactions is proportional to V_W, whereas the contribution of strong intermolecular interactions of functional groups at their fixed number in a molecule is independent of V_W.

Over the entire *n*-alkane homologous series T_b increases with V_W (Fig. 1, plot *1*). The same trend is characteristic of the first members of the triglyceride [up to the C_4 homolog (butyric triglyceride)] and anhydride [up to the C_8 homolog (caprylic anhydride)] homologous series. However, in going from the C_4 to C_6 homolog (caproic triglyceride), a sharp (more than 100°C) fall of T_b (Fig. 1, plot ; Table 1) is observed; the same fall of T_b is observed in the anhydride series in going from the C_8 to C_{10} (capric anhydride) homolog (Fig. 1, plot *3*; Table 2). The “well” in both the homologous series shows up at roughly the same Van der Waals molecular volumes (V_W ~350–400 Å^3). On further increase in the molecular size of triglycerides (anhydrides), T_b again, after the “well”, begins to increase along the homologous series (Fig. 1, plots *2* and *3*).

The observed trend in variation of T_b over the triglyceride and anhydride homologous series is difficult to explain not invoking the concept that the molecules of these compounds undergo compacting when their $CH_3(CH_2)_n$ alkyl fragments attain a certain size, and, therewith, part of intermolecular bonds convert into intramolecular [2].

Actually, since at a fixed molecular size (V_W) the overall number of contacts (intermolecular and intramolecular) remains constant, intramolecular interaction develops at the expense of the corresponding intermolecular interaction, which renders the latter interaction weaker and thus decreases T_b. The increase of T_b after the “well” apparently implies complete screening of the ester (anhydride) groups with the hydrocarbon fragments of the molecules, and the further enhancement of intermolecular interactions and increase of T_b are provided by weak (dispersion) interactions involving increasing number of CH_2 units.

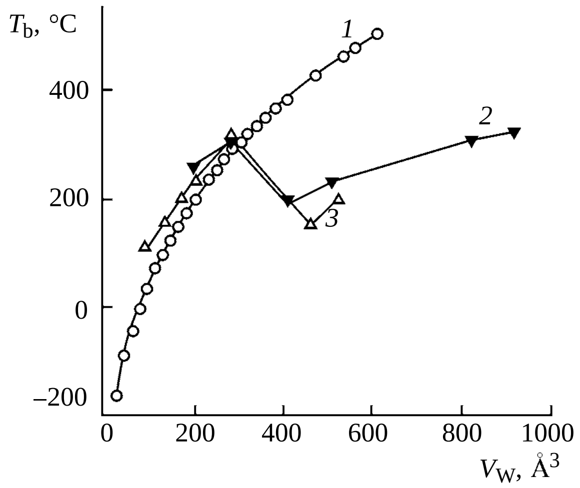

Fig. 1. Plots of T_b vs. V_W. (*1*) *n*-Alkanes, (*2*) triglycerides, and (*3*) anhydrides.

Convincing evidence for the proposed interpretation of the observed anomalous trend in T_b comes from the results of computer modeling of associative structures of triglycerides and anhydrides. Actually, the modeling results in more and more compact molecular shapes as the number of CH_2 groups in the molecules of triglycerides and anhydrides is increased (Figs. 2 and 3): from unpuckered conformations of the initial members to a puckered compact conformation of higher members of homologous series. Stability of the compact molecular shape of triglycerides and anhydrides in their ordered associates with a regular arrangement of molecules should depend on the length of the hydrocarbon fragments: The longer is the hydrocarbon chain, the more stable is the compact conformer. Actually, the compact molecules of lower triglycerides (up to C_4) and anhydrides (up to C_8) unfold their hydrocarbon chains on association, thereby converting intermolecular interactions of the latter into intermolecular. By contrast, the molecules of higher homologs (C_6 and C_{10} and higher) preserve their compact puckered conformation. The formation of ordered associates is accompanied by entropy decrease ($\Delta S < 0$). In such process, the Gibbs energy ΔG will decrease ($\Delta G < 0$) only when $\Delta H < 0$ and $|\Delta H| > |T\Delta S|$, i.e. the enthalpy change should be

Table 1. Van der Waals molecular volumes (V_W), boiling points (T_b), energies of intermolecular interactions (E_{IMI}), standard enthalpies of vaporization (ΔH_v^0), and fractions of intermolecular bonds (α_{IMI}) for triglyceride homologs

Triglyceride		V_W, Å^3	T_b, °C	T_b^c,[a] °C	E_{IMI}, kJ/mol	ΔH_v^0, kJ/mol	α_{IMI}
$CH_3(CH_2)_nCOOH$	n						
Acetic	0	199.7	260	241	56.6	88.2	0.64
Propionic	1	251.0	–	272	64.9	102.4	0.63
Butyric	2	302.3	310	295	65.2	116.6	0.56
Valeric	3	353.6	–	202	57.6	130.8	0.44
Caproic	4	404.9	200	212	58.1	145.0	0.40
Enantic	5	456.2	–	230	69.2	159.3	0.43
Caprylic	6	507.5	233	250	77.6	173.5	0.44
Capric	8	610.1	–	278	82.0	201.9	0.44
Lauric	10	712.7	301	321	113.7	232.5	0.49
Myristic	12	815.3	311	342	140.0	258.8	0.54
Palmitic	14	917.9	320	361	157.0	287.2	0.54
Stearic	16	1020.5	–	385	172.0	309.6	0.55

[a] T_b^c, calculated boiling point. The relative errors in T_b^c were 2.5–7.0% of experimental T_b.

Table 2. Van der Waals molecular volumes (V_W), boiling points (T_b), energies of intermolecular interactions (E_{IMI}), standard enthalpies of vaporization (ΔH_v^0), and fractions of intermolecular bonds (α_{IMI}) for anhydride homologs

Angidride		V_W, Å^3	T_b, °C	T_b^c,[a] °C	E_{IMI}, kJ/mol	ΔH_v^0, kJ/mol	α_{IMI}
$CH_3(CH_2)_nCOOH$	n						
Acetic	0	93.3	140	132	43.6	44.2	0.99
Butyric	2	161.7	198	185	59.4	63.2	0.99
Caproic	4	225.7	241	235	64.5	65.2	0.99
Caprylic	6	298.5	285	274	69.2	69.9	0.99
Capric	8	366.9	—	160	77.7	120.1	0.64
Lauric	10	435.3	—	171	81.6	130.7	0.62
Myristic	12	503.7	166	183	84.2	139.0	0.60
Pentadecanoic	13	544.8	—	194	90.0	148.5	0.61
Palmitic	14	591.5	198	224	92.3	158.0	0.58
Stearic	16	655.1	—	252	100.1	177.0	0.56

[a] T_b^c, calculated boiling point. The relative errors in T_b^c were 2.0–5.0% of experimental T_b.

larger in absolute value than the product $T\Delta S$. This condition, as judged from the results of computer modeling of associative structures, is met in the triglyceride homologous series beginning with the C_6 homolog and in the anhydride homologous series beginning with the C_{10} homolog, i.e. when compact molecular conformations are preserved in associates.

We calculated energies of intermolecular interactions (E_{IMI}) and standard enthalpies of vaporization (ΔH_v^0) for all the homologs studied (Tables 1, 2). It was of interest to correlate the energy of intermolecular interactions, giveb by molecular dynamics calculations, and the enthalpies of vaporization of the corresponding compounds, calculated by the procedure in [10]. The enthalpy of vaporization at temperatures and pressures other than zero is lower than the energy of intermolecular interactions, which is calculated at zero temperature and pressure, but E_{IMI} for associates containing a finite number of molecules is lower than the energy of intermolecular interactions of a compound, because the former values involve uncompensated contributions of molecules present on the associate surface. At the same time, as E_{IMI} increases monotonically with increasing associate size, then such number of molecules in the associate may

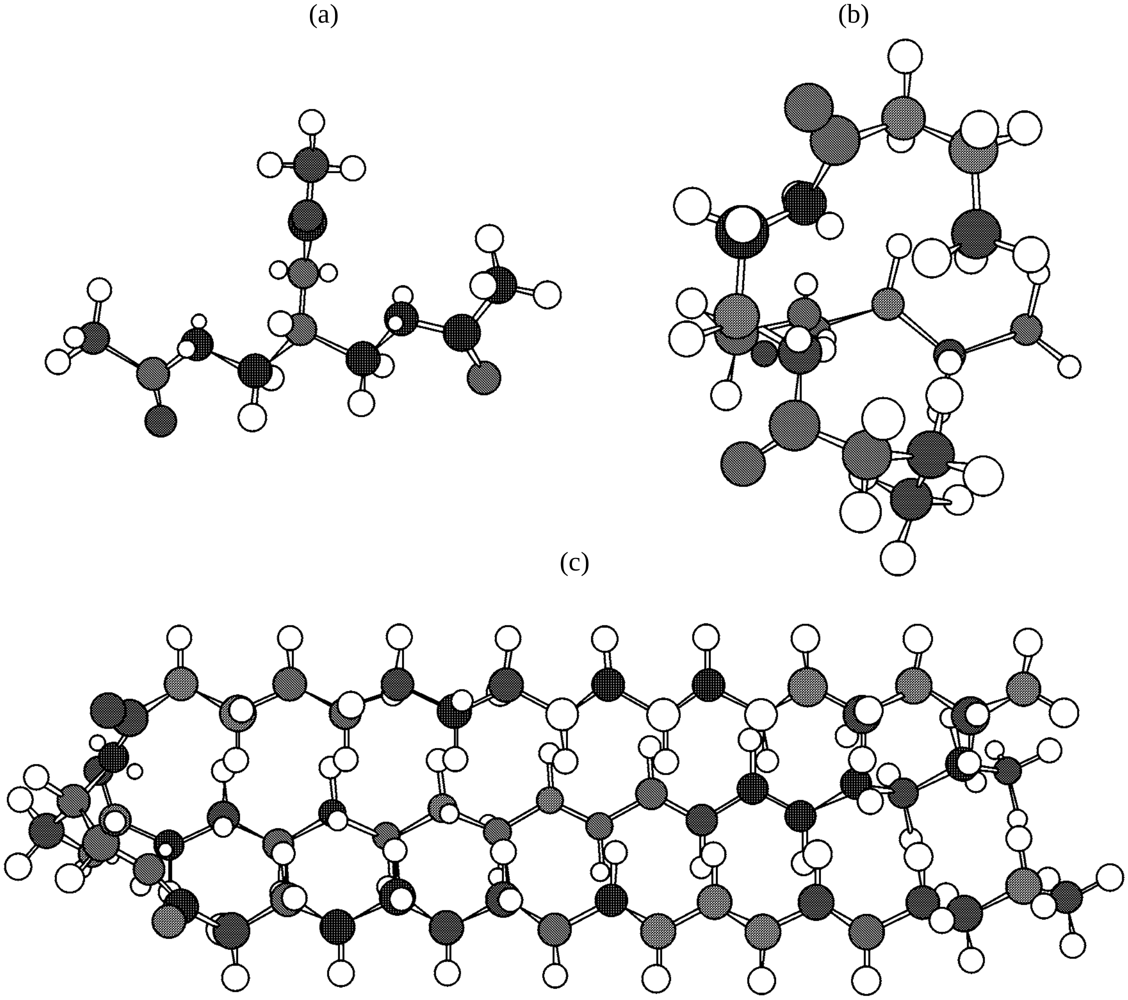

Fig. 2. Triglycerides of monocarboxylic saturated acids at minimum potential energy. Homolog: (a) C_2, (b) C_4, and (c) C_{18}.

by found, at which E_{IMI} best fits the standard enthalpy of vaporization of the corresponding compound, and to find correlation for E_{IMI} for the other compounds. Actually, as established in [4], for structurally diverse hydrocarbons up to C_8, ethers and esters, as well as other functionally substituted organic compounds with alkyl fragments up to C_6, the divergence between E_{IMI} and ΔH_v^0 is generally 1–4%. However, in the triglyceride homologous series, E_{IMI} is lower than ΔH_v^0 by 40–60% (Table 1), while in the anhydride homologous series, by about 40% beginning with C_6 (Table 2). Calculation of E_{IMI} by increments, i.e. contributions of atomic groups [10], suggests that the latter all are involved in intermolecular interactions. By contrast, molecular mechanics calculations of E_{IMI} [4] include the preferred molecular conformation only, i.e. atomic groups directly involved in intermolecular interactions. This allows estimation of the fraction of realized energy of intermolecular interaction in the total potentially possible energy of such interaction from the $E_{IMI}/\Delta H_v^0 = \alpha_{IMI}$ ratio.

The coefficients of intermolecular interactions (α_{IMI}) for the triglyceride and anhydride homologous series are listed in Tables 1 and 2. In the anhydride homologous series up to C_8, virtually all physical bonds, as judged from the α_{IMI} values (0.99), are realized intermolecularly, and T_b increases with enhancing dispersion intermolecular interactions of the lengthening $CH_3(CH_2)_n$ hydrocarbon chains. In the triglyceride homologous series, already the first members of the series up to the C_4 homolog ($\alpha_{IMI} \approx 0.6$), a considerable part of intermolecular interactions is converted into intramolecuar, whereas the increase of T_b, too, is provided by enhancing dispersion intermolecular interactions of the lengthening hydrocarbon fragments of the molecules. The sharp decrease of α_{IMI} for triglycerides in going from the C_4 to C_6 homolog and for anhydrides in going from the C_8 to C_{10} homolog results in a catastrophical fall of T_b by more than 100°C (Tables 1 and 2).

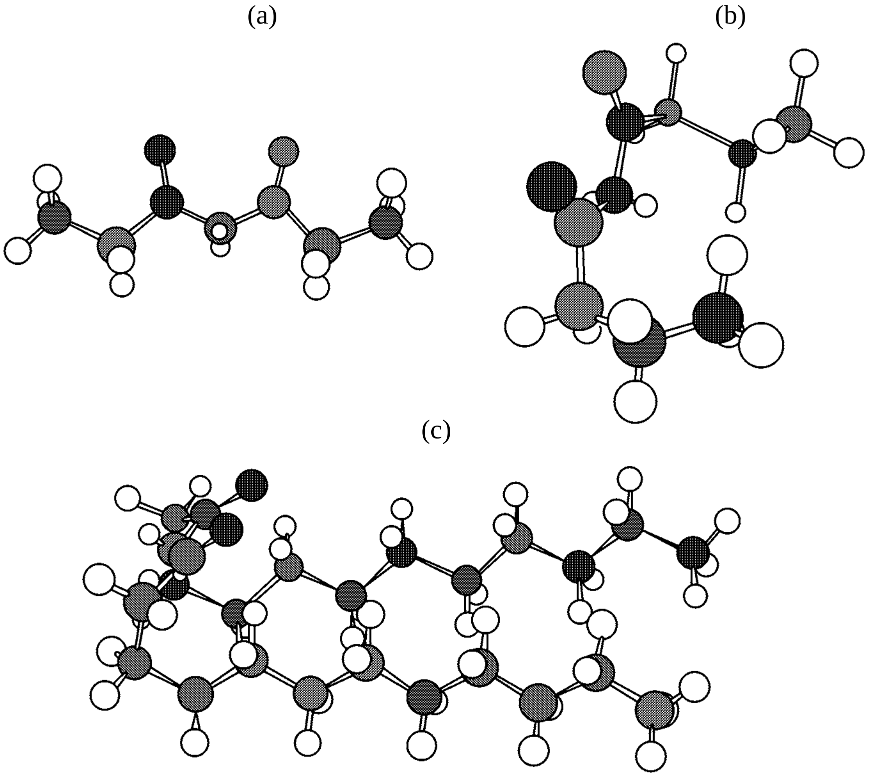

Fig. 3. Anhydrides of monocarboxylic saturated acids at minimum potential energy. Homolog: (a) C_2, (b) C_4, and (c) C_{12}.

Probably, the hydrocarbon fragments in the caproic triglyceride (C_6 homolog) and capric anhydride (C_{10} homolog) have attained such a size that they screen the centers of strong intermolecular interactions COO and OCOO. With further lengthening of the hydrocarbon chain after it has attained the critical size, the T_b of triglycerides and anhydrides increases again (Tables 1 and 2) due to weak (dispersion) forces of the increasing number of CH_2 units. This increase in higher triglyceride homologs is accompanied by a certain increase of the fraction of intermolecular interactions, while in higher anhydride homologs the respective contribution does not change (Tables 1 and 2).

The validity of differentiation between inter- and intramolecular interactions in triglycerides and anhydrides by the α_{IMI} criterion is confirmed by the fact that the boiling points of these compound calculated with allowance for α_{IMI} (T_b^c) nicely fit experiment (reference T_b).

The T_b^c values were calculated in terms of the model of pair reversible interactions of like atomic groups [11]. This model describes associate formation as a process of interaction of a labile system of intermolecular physical bonds with a limited lifetime τ of physical nodes, which evolves with increasing temperature to lower τ and volume concentration of nodes (ν/ν_0).

$$\tau = (K_{01})^{-1}\exp(\alpha_{IMI}\Delta H_v^0/RT), \quad (1)$$

$$\nu/\nu_0 = (1 + 1/8K_2\nu_0\tau) - [(1 + 1/8K_2\nu_0\tau)^2 - 1]^{1/2}. \quad (2)$$

Here ν_0 is the limiting concentration of intermolecular bonds of a given type, realized on binding of all initial atomic groups G into associate G_2.

$$G + G \underset{K_1}{\overset{K_2}{\rightleftarrows}} G_2.$$

$K_1 = K_{01}\exp(-E_1/RT)$ and $K_2 = K_{02}\exp(-E_2/RT)$ are the rate constants of monomolecular decomposition (dissociation) and bimolecular regeneration (association) of intermolecular bonds of the given type and ν/ν_0 is, in physical meaning, the equilibrium association degree of atomic group G at a given temperature.

The model based on molecular physics data allows calculation of the molecular association index $\bar{\varphi}_T$, i.e. the mean number of intermolecular bonds formed by a molecule at temperature T.

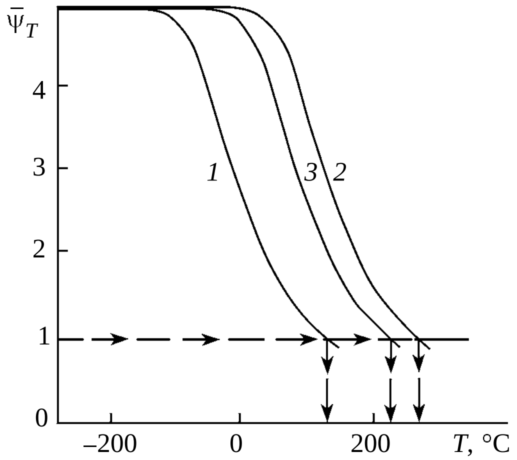

Fig. 4. Plot of molecular association index $\bar{\varphi}_T$ vs. temperature for (*1*) acetic, (*2*) caprylic, and (*3*) palmitic anhydrides.

$$\bar{\varphi}_T = \sum_{i=1}^{k} n_i(\nu/\nu_0)_i. \quad (3)$$

Here n_i is the number of like atomic groups G in the molecule; $(\nu/\nu_0)_i$ is the fraction of atomic groups of a given type, formed associative bonds at temperature T; and k is the number of unlike atomic groups in the molecule.

For all the triglyceride and anhydride homologs from C_2 to C_8 we constructed $\bar{\varphi}_T = f(T)$ plots (Fig. 4).

Equation (3) was used to calculate molecular association indices at $T_b(\bar{\varphi}_k)$ for the homologous series of 16 classes of organic compounds with unbranched hydrocarbon chains, including anhydrides and esters. It was found that each organic compound boils at a temperature that corresponds to a decrease of $\bar{\varphi}_T$ (decay function of temperature) to a well-defined and the same for all the compounds $\bar{\varphi}_k$ value. Depending of the numerical values of parameters chosen for quantitative description of intermolecular interactions, the most probable absolute value of $\bar{\varphi}_k$ is 0.05–1.

Taking $\bar{\varphi}_k = 1$, by $\bar{\varphi}_T = f(T)$ curves like those in Fig. 4, we obtain T_b^c for each of the triglycerides and anhydrides studied. The resulting data are listed in Tables 1 and 2. The T_b^c values fit experimental within 3–7%. If intermolecular interaction coefficients are allowed for, the divergence between T_b^c and T_b is 40–60%. This result provides evidence for the adequacy of the model of pair reversible interactions of like atomic groups and the validity of differentiation between inter- and intramolecular interactions by the α_{IMI} criterion.

Thus, together the resulting data give us grounds to beleive that intermolecular interactions in triglycerides and anhydrides are partly converted into intramolecular, which results in anomalously low T_b values and abrupt fall of these values over the homologous series of these compounds. The same effect would be expected in organic compounds of other classes.

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