MOLECULAR AND CRYSTAL STRUCTURE OF α,ω-BIS(METHACRYLOYLETHYLENEGLYCOL)-PHTHALATE

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The compound α,ω-bis(methacryloylethyleneglycol)phthalate is synthesized and its molecular structure is determined. The packing of the molecules can be used as a model for association of oligoacrylate esters in the liquid phase.

The lack of data on the structure of polymerizing compounds makes study of polymerization mechanisms difficult. One method for solving this problem is to use single crystal x-ray studies to find the monomer or oligomer structure in the crystal. These data can be used to examine liquid-phase processes. In the present work, such an approach is used to judge the structural aspects of α,ω-bis(methacryloylethyleneglycol)phthalate (I) polymerization. A general view of the crystal structure of (I) is shown in Fig. 1. Bond lengths and principal bond angles are given in Fig. 2. The conformation of (I) in the crystal was characterized qualitatively. Three planar fragments in it can be arbitrarily separated: C^1—C^6 (fragment 1), $C^7O^1O^2C^8$ (fragment 2), and $C^{14}O^5O^6C^{15}$ (fragment 3) (the maximal deviation of atoms from the mean square planes is 0.014 Å). Two terminal fragments rotated relative to each other are also identified: $C^9O^3C^{10}O^4C^{11}C^{12}C^{13}$ (4) and $C^{16}O^7C^{17}O^8C^{18}C^{19}C^{20}$ (5) (maximal deviations of the atoms from coplanarity are 0.026 and 0.092 Å, respectively). The dihedral angles between the averaged planes of these fragments are: 1/2, 10.9; 1/3, 96.9; 2/4, 102.9; and 3/5, 124.7°. The torsion angles are: $C^2C^1C^7O^2$, 171.86; $C^1C^7O^2C^8$, 175.63; $C^7O^2C^8C^9$, 173.39; $O^2C^8C^9O^3$, −72.91; $C^8C^9O^3C^{10}$, −174.11; $C^9O^3C^{10}C^{11}$, 178.36; $O^3C^{10}C^{11}C^{13}$, −2.06; and $C^1C^2C^{14}O^6$, −83.36; $C^2C^{14}O^6C^{15}$, 177.04; $C^{14}O^6C^{15}C^{16}$, 159.94; $O^6C^{15}C^{16}O^7$, 61.29; $C^{15}C^{16}O^7C^{17}$, 174.53; $C^{16}O^7C^{17}C^{18}$, 172.06; $O^7C^{17}C^{18}C^{19}$, −177.09°.

The bond lengths obtained (Fig. 2) are similar to the statistical average for the corresponding bonds in organic compounds [1] with the exception of the C^{18}—C^{19} bond, 1.405(4) Å, and the C^{18}—C^{20} bond, 1.404(4) Å, in one of the methacrylate fragments. These values lie between the standard lengths for $C_{sp^2}{=}C_{sp^2}$ $(C{-}\overset{\diagdown}{C}{=}CH_2)$ and $C_{sp^3}{-}C_{sp^2}$ $(CH_3{-}\overset{\diagdown}{C}{=}C)$ (1.321 and 1.503 Å [1]). However, the C^{11}—C^{12}, 1.330(3) Å and C^{11}—C^{13}, 1.487(3) Å bond lengths in the other methacrylate fragment are close to these standard values. This most likely indicates disordering in the CH_2 and CH_3 groups of the first methacrylate fragment over two positions differing by rotation around the C^{17}—C^{18} bond by 180° (Fig. 1). The larger thermal parameters for C^{19} and C^{20} compared to C^{12} and C^{13} also suggest such disordering.

Molecules of (I) are packed such that the ester groups of neighboring molecules are directed toward each other. The planar fragments $H_2C{-}O{-}C(O)C(CH_3){=}CH_2$ are superimposed, forming stacks along the *a* axis (Fig. 1). The average planes of the superimposed fragments are approximately parallel (5.3° angle between them) and are separated by ~3.8 Å. Normals to the planes deviate slightly from the *a* axis. Each atom of the methacrylate fragment of one molecule (except the CH_3 group) is positioned over (under) a particular atom of the neighboring methacrylate. In each successive "layer," the atoms change to the opposite order and only atoms of the carbonyl groups do not change their relative position. (See top of following page.)

The methylene groups, due to the disorder noted above, are either cis relative to the carbonyl and form the "backbone" of the stack or are trans to it and the methyl groups form the "backbone."

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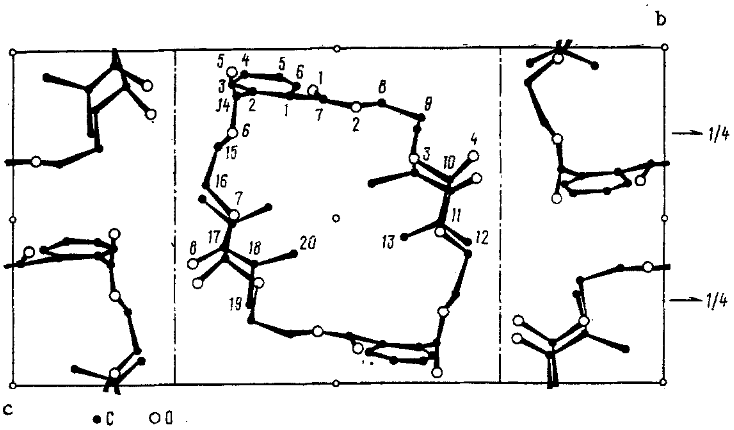


Fig. 1

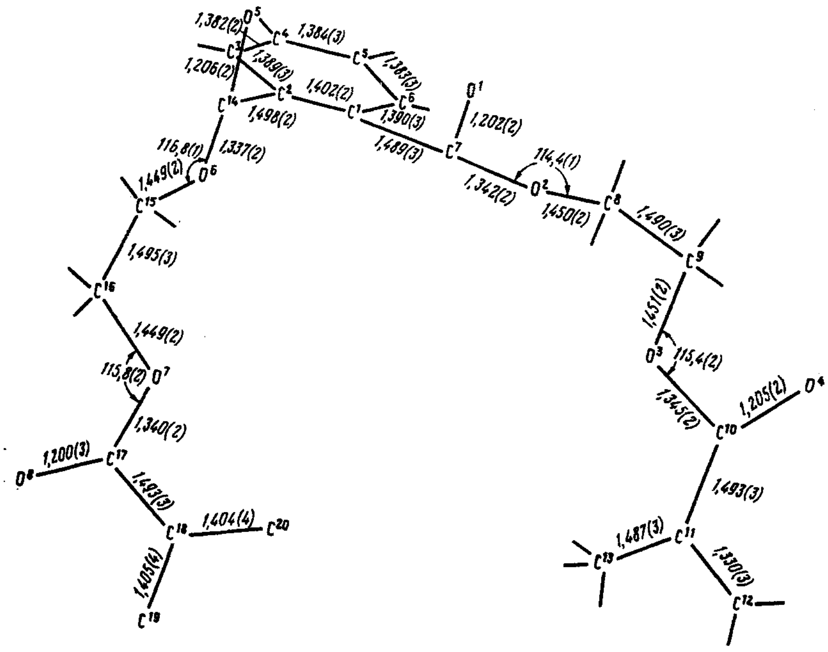
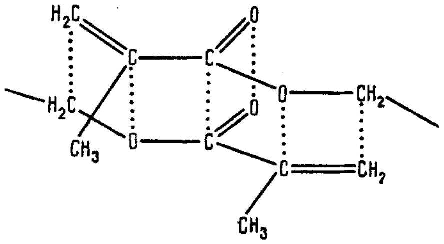
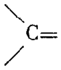
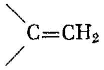


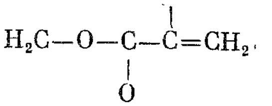
Fig. 2

Fig. 1. Projection of the structure of (I) on the bc plane.

Fig. 2. Bond lengths (Å) and principal bond angles (deg) in (I).



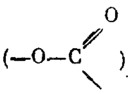
The intermolecular association is important in polymerization of the methacrylic monomers [2]. Thus, it is interesting to compare the crystal structure of (I) with data for the structure of similar liquid-phase associates. In [3], changes in the PMR spectra of methylmethacrylate (MMA) and α,ω-methacrylbis(triethyleneglycol)phthalate (MGP-9) on adding various solvents were studied. Selective shifts δ were seen for the signals of the protons of the CH_2 group in hexane, the protons of the CH_2 and CH_3 groups in acetonitrile, and the protons of all groups in benzene. Formation of rigid rod-like molecular associates with carbonyl groups on the axes and CH_2 groups on the periphery was proposed on the basis of these data. The CH_2 groups were proposed to be capable of binding the associates to each other [3]. A study of the ^{13}C NMR spectra of triethyleneglycol dimethacrylate (TGM-3) showed that the spin-lattice relaxation time of all C atoms of the TGM-3 decreased on adding finely dispersed TGM-3 polymer. The motion of atoms C=, , CH_2=, and CH_3– changes least [4]. This effect was also related to the formation of TGM-3 associates according to the model proposed in [3]. However, the correspondence of this model to the observed decrease in motion of the atoms of the  group compared to the decreased motion of the carbonyl C atom was not discussed.

The packing of (I) in the crystal agrees well with the results given in [3, 4]. The  $H_2C{-}O{-}\underset{\underset{O}{|}}{C}{-}\overset{|}{C}{=}CH_2$ groups of the stack "backbone" in (I) are analogous to the methacrylate fragment of TGM-3. These lose the most motion on association in the liquid. The carbonyl groups in the stacks are superimposed one over the other. A part of the methylene groups lie on the stack periphery due to the disordering mentioned above. Therefore, the packing of (I) and association of methacrylate monomers in the liquid are caused by interaction of the same atomic fragments. This suggests that the mode of association of (I) in the crystal is characteristic of association of methacrylate monomers (oligoacrylate esters) and can be used to model their structure in the liquid. Evidently, the active double bonds are far from each other with such binding. This excludes polymerization without decomposition of the associates, i.e., such a model describes only kinetically inactive associates.

In our opinion, the present results can be used to construct a model for polymerization of an oligoacrylate ester considering only the kinetically inactive associates.

EXPERIMENTAL

Chromatographic monitoring was carried out on a Tsvet-306 instrument (λ 274 nm).

α,ω-Bis(methacryloylethyleneglycol)phthalate (I). To a solution of 37.84 g (0.186 mole) phthaloyl chloride and 48.7 g (0.372 mole) ethyleneglycol monomethacrylate in 100 ml benzene with stirring were added dropwise 32 ml (0.4 mole) Py in 40 ml benzene. The mixture was heated for 5 h at gentle reflux. The precipitate formed was filtered off. A viscous oil (I) (72 g, 98%) with n_D^{20} 1.5087-1.5092 was obtained after removal of solvent. The oil crystallized on cooling, mp 40-42°C (from ethanol). Found, %: C 61.52; H 5.96. Mol. wt. = 360. $C_{20}H_{22}O_8$. Calculated, %: C 61.53; H 5.64. Mol. wt. = 390. IR spectrum (ν, cm^{-1}): 1720 (C=O), 1630 (C=C), 1360-1370 ($-CH_3$), 1720 and 1280 (), 1140-1180 (C–O). The purity of (I) was confirmed by HPLC.

The x-ray structure used a Syntex $P2_1$ diffractometer (λ Mo Kα, −120°C, θ/2θ scanning between $2 \leq 2\theta \leq 50°$, 3689 measured reflections of which 2947 with $I > 2\sigma$ were used to solve and refine the structure). Crystals of (I) are monoclinic, a = 7.771(4), b = 23.02(1), c = 11.629(7) Å, β = 102.25(5)°, Z = 4, d_{calc} = 1.28 $g \cdot cm^{-3}$, space group $P2_1/n$. The structure was solved by direct methods using MULTAN and was refined by anisotropic (for nonhydrogen atoms) full-matrix least squares. Disorder of the CH_2 and CH_3 groups (atoms C^{19} and C^{20}) on one of the terminal fragments was seen during refinement. All H atoms (except those of the disordered CH_2 and CH_3 groups) were located in a difference synthesis. Their positions were refined with fixed isotropic thermal parameters (B_{iso} = 5 $Å^2$). The final R factor was 0.038. All calculations were carried out using the YANX programs [5].

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CALCULATION OF RETENTION INDEXES OF ALKYLOXAZOLES AND ALKYLTHIAZOLES IN CAPILLARY CHROMATOGRAPHY

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The retention indexes of 41 alkyloxazoles and alkylthiazoles have been determined at 110°C on capillary columns with OV-101/KF, Triton X-305/KF, and PEG-40M/KF, and the contributions calculated to the retention indexes of the methyl, ethyl, and propyl groups at different positions in the rings. The magnitude of the contribution for each alkyl group depends on its position in the ring; this has been used in the calculation schemes to predict the retention indexes of di- and trisubstituted oxazoles and thiazoles with different alkyl radicals.

At present files of gas chromatographic (GC) data are being compiled for the identification of components of complex mixtures of organic substances with the use of a computer. The review [1] shows that computer programs, based on structure-sorption correlations, can significantly widen the range of identified substances. The provision of programs of this kind for the determination of heterocyclic compounds meets with a number of difficulties, caused by the absence of established rules governing the changes in the GC retention characteristics. This requires the systematic study of the GC behavior of individual series of heterocyclic compounds. The change in the sorption energy of N-, S-, and O-containing cyclic compounds as a function of the structure of their molecules has been investigated recently. It has been shown that, when a CH_3 group is in the immediate vicinity of any heteroatom, a significant decrease in the energy of van der Waals interactions of the compound with the stationary phase of any polarity is observed, in comparison with a substance in which the methyl group is located at a distance from the heteroatom [2-4]. By taking this into account it was possible to calculate the retention indexes of methyl-substituted pyridines and pyrazines in capillary chromatography with satisfactory precision [5].

Alkyloxazoles and alkylthiazoles are important components of the smell of many food products [6]. The possibility of calculating the retention indexes for these compounds at the conditions of capillary chromatography has not been explored. The described principle of nonlinear change of sorption energy [2, 4] has only been used to determine the retention indexes of alkylthiazoles on packed columns [7].

The objectives of the present study under the conditions of gas chromatography were: 1) to determine and to compare the contributions of methyl, ethyl, and propyl groups to the values of the retention indexes of alkyloxazoles and alkylthiazoles as functions of the position of the alkyl group in the ring and of its proximity to the heteroatoms N, S, and O; 2) to establish schemes for the calculation of retention indexes of di- and trisubstituted alkyloxazoles and alkylthiazoles, based on the principle of nonadditive contributions of equal alkyl groups in substituted heterocycles; 3) to verify experimentally the schemes for the calculation of the retention indexes for alkyloxazoles and alkylthiazoles, analyzed on capillary columns of different polarity.

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