OPTICAL STUDY OF THE CONFORMATIONS OF 2-METHYL-1-OXYCYCLOHEXYLETHYLENE OXIDES

![structural formulas I-IV](image)

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structural formulas I-IV

Figure 1: structural formulas I-IV

Abstract

Full Text

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OPTICAL STUDY OF THE CONFORMATIONS OF 2-METHYL-1-OXYCYCLOHEXYLETHYLENE OXIDES

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In the oxidation of cis-2-methyl-1-vinylcyclohexanol with peracetic acid in chloroform, one of us (^{1}) isolated two glycidic alcohols with cis configuration, and in the oxidation of trans-2-methyl-1-vinylcyclohexanol, two glycidic alcohols with trans configuration were obtained (the reactions proceed with retention of configuration at the asymmetric center). It was proposed that, in each pair, the alcohols differ from one another in the spatial position of the oxirane ring and are diastereoisomers, i.e., that the following four glycidic alcohols had been obtained: (I) cis-erythro-(2-methyl-1-oxycyclohexyl)-ethylene oxide, (II) cis-threo-(2-methyl-1-oxycyclohexyl)-ethylene oxide, (III) trans-erythro-(2-methyl-1-oxycyclohexyl)-ethylene oxide, (IV) trans-threo-(2-methyl-1-oxycyclohexyl)-ethylene oxide:

All four alcohols have very different melting points: one of the alcohols of the cis series has m.p. 43-43.5°, the other is a liquid (its b.p. 89-90° (7 mm)); one of the alcohols of the trans series has m.p. 75-75.5°, the other 40.5-41°.*

The study of the spectra of combination scattering of light of the glycidic alcohols obtained makes it possible to continue clarifying the question of their structure. This study showed that the hydroxyl group in all four alcohols in the liquid state is involved in a hydrogen bond with the oxygen atom of the oxirane ring: the O—H frequency is smeared into a band (see Table 1). In the two trans isomers this band is substantially different: in the isomer with the lower melting point (40.5-41°) it is narrow (~45 cm^{-1}), with only a weak smearing of it in intensity toward the low-frequency side; in the isomer with the higher melting point (75-75.5°) it is broader (~200 cm^{-1}) and of comparatively uniform intensity over its entire width. This indicates (^{3}) the unquestionable predominance in the first of the two trans isomers of an intramolecular hydrogen bond, and in the other of an intermolecular one, i.e., that the first is compound (IV) (m.p. 40.5-41°), and the other is compound (III) (m.p. 75-75.5°). Apparently, precisely this difference in the types of hydrogen bonding has a substantial effect in this case on the differences in melting points. If the large difference in melting points of the two glycidic alcohols of the cis series is due to the same cause, then one of these alcohols with the higher melting point, likewise caused in this case by intermolecular hydrogen bonding, is compound (I) (m.p. 43-43.5°), and the other—the liquid with an intramolecular hydrogen bond—is compound (II). The optical data confirm this: in (II), on the high-frequency side of the O—H band, there is sharply distinguished and even somewhat separated from the remaining

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* For the study of the nuclear magnetic resonance of these substances, see (2).

Table 1

Frequencies of vibrations of the hydroxyl, oxide ring, and cyclohexane ring (in cm^{-1})

Groups	Liquid state (I)	Liquid state (II)	Liquid state (III)	Liquid state (IV)	20% solution in CCl_4 (I)	20% solution in CCl_4 (II)	20% solution in CCl_4 (III)	20% solution in CCl_4 (IV)
O—H	3390—3570; band	3520—3565; 3390—3520; bands	3390—3590; band	3520—3565; band	3541 (1*)3565 (2*)3612 (0)3621 (1)	3525 (1*)3552 (2*)3612 (0)3623 (0)	3542 (1*)3563 (3*)3613 (0)3621 (0)	3527 (1*)3550 (2*)3613 (0)3626 (0)
Oxide ring	1250 (2*)1257 (9*)1268 (2* dbl)	1252 (2* dbl)1265 (9* dbl)	1252 (7 dbl)1268 (1 dbl)	1252 (1 dbl)1269 (6 dbl)	1249 (1*)1255 (5*)1269 (1 dbl)	1252 (1* dbl)1264 (5* dbl)	1252 (5 dbl)1268 (0 dbl)	1253 (1 dbl)1269 (4 dbl)
Cyclohexane ring	703 (8 dbl)714 (2 dbl)	702 (8 dbl)713 (3 dbl)	700 (1 dbl)718 (7 dbl)	703 (1 dbl)716 (8 dbl)	700 (4 dbl)714 (1 dbl)	701 (4 dbl)715 (2 dbl)	701 (1 dbl)719 (4 dbl)	699 (1 dbl)715 (4 dbl)

* With slight broadening toward the low-frequency side.

···part of the band, a narrow intense band at ~ 3520—3565 cm^{-1}, indicating the predominance in (II) of an intramolecular hydrogen bond, in contrast to (I), in which, owing to the predominance of intermolecular hydrogen bonding, no such sharp separation of a similar band is observed. But, unlike the threo isomer (IV), in the threo isomer (II) the low-frequency part of the band (~ 3390—3520 cm^{-1}) is also sufficiently intense. This indicates that in the liquid state, in (II), the O—H group in a fairly large fraction of the molecules is released from the intramolecular hydrogen bond and enters into an intermolecular one, i.e., the threo isomer partially passes into the erythro isomer, or into a form close to it in the position of the oxide ring. In (I) the transition of the erythro isomer into the threo isomer is almost not detected optically.

As can be seen, the principal stabilizing factors in the case under consideration of erythro-threo isomerism are two kinds of hydrogen bonds. The energy of these bonds is small (~ 3 kcal/mole). Therefore they cause a sharp difference between the erythro-threo isomers in the crystalline state of the alcohols studied, but under the conditions of our experiment (liquid state at $\sim 30°$ for (II) and at $\sim 85°$ for (III); supercooled liquid state at $\sim 30°$ for (I) and (IV); irradiation under the experimental conditions by quanta of light in the blue and near-ultraviolet regions), the stabilizing influence of the hydrogen bonds is weakened. However, short-range order is preserved under these conditions as well, and the structural features specific for each of the alcohols studied, as erythro and threo isomers, remain predominant.

In 20% solutions of the alcohols studied in CCl_4* intramolecular hydrogen bonds, as a rule, are not destroyed (^{3}); optically this is confirmed by the retention, in the former region, of the narrow hydroxyl-frequency band in (II) and (IV). The numerous complexes associated by means of intermolecular hydrogen bonding in (I) and (III) are destroyed, but even under these conditions obviously dimeric complexes (short-range order) are still preserved in them; monomers also appear. Optically this is confirmed by the disappearance of the broad O—H band, the appearance of a narrow band in the region ~ 3540—3565 cm^{-1}, and weak doublets of the O—H frequencies of individual molecules: ~ 3612, 3621 cm^{-1}. The narrow bands mentioned are also doublets. According to our previous investigations (see references to them in (^{4})), the higher frequency in each of these doublets characterizes an axial hydroxyl, the lower one an equatorial hydroxyl. In almost all the isomers the higher frequencies in the O—H doublets are more intense; only in (II) are the intensities of the two frequencies approximately equal. All this indicates that each of the fo—

* The intensities of the frequencies of the solutions are not comparable with the intensities of the frequencies of the alcohols studied in the liquid state: the solutions were recorded with a considerably longer exposure.

···alcohols under the experimental conditions exists in two conformations, of which the more favored are the conformations (designated according to the largest substituents—the oxirane ring and the methyl group): for (I), cis-*ea*; for (III) and (IV), trans-*ee*; for (II), both conformations are present in approximately equal amounts (see Fig. 1).

In the spectrum of ethylene oxide the oxirane ring is characterized by the frequency of the puckering vibration of the three-membered ring, 1269 cm^{-1} (^{5}). The oxirane ring is characterized by approximately the same frequency (within 1264—1269 cm^{-1})

Fig. 1

Figure 2: Fig. 1

Fig. 1

in the spectra of the threo isomers (II) and (IV); in the spectra of the erythro isomers (I) and (III) this frequency is somewhat lowered, lying in the range 1252 –1257 cm^{-1} (see Table 1). The retention in the spectra of the threo isomers of a frequency of reduced intensity ~ 1252 cm^{-1}, and in the spectra of the erythro isomers of a frequency of reduced intensity ~ 1269 cm^{-1}, indicates that under the conditions of our experiment the erythro and threo isomers are to some extent converted into one another.

The doublet character of the lines indicates the existence of the alcohols in two conformations. In the spectrum of (I) the doublet 1250, 1257 is resolved quite distinctly.

In the spectra of the alcohols studied (see Table 1), in the frequency region of the puckering vibration of the ortho-substituted cyclohexane ring (~ 700–720 cm^{-1}), one double, more intense frequency is observed and another, likewise double, frequency sharply weakened in intensity. According to our previous investigations (^{6}), compounds (I) and (II), with intense lower frequencies of the ring puckering vibration (~ 699–703 cm^{-1}), have the cis configuration, whereas compounds (III) and (IV), with an intense higher frequency of this vibration (~ 713–719), have the trans configuration. The frequencies weakened in intensity indicate the presence of an admixture of one configuration in the other (especially in (II)). The double nature of the frequencies considered indicates that each of the alcohols under the experimental conditions exists in two conformations, as noted in Fig. 1.

Combination light-scattering spectra were recorded on the domestic ISP-51 spectrograph with a medium camera and on a Hilger E612 spectrograph from the exciting blue line 4358 Å of a mercury lamp (for intensity designations see (4)).

(I) cis-erythro-(2-methyl-1-oxycyclohexyl)-ethylene oxide, $\Delta\nu$ cm^{-1}: 181 (2*), 192 (3*), 199 (2*), 263 (1**), 276 (0**), 287 (3), 303 (1), 323 (2), 371 (2*), 387 (4*), 395 (4*), 408 (0), 452 (5), 485 (6), 509 (0), 530 (4), 539 (0), 551 (6 dv), 566 (0), 586 (4 dv), 703 (8 dv), 714 (2 dv), 787 (7), 812 (4*), 825 (4*), 839 (4), 861 (6), 875 (4), 895 (3*), 904 (4*), 945 (5**), 956 (5**), 982 (6*), 992 (2*), 1004 (7*), 1057 (3**), 1085 (5**), 1135 (6), 1144 (0), 1161 (6), 1181 (3 dv), 1223 (2 sh), 1250 (2*), 1257 (9*), 1268 (2* dv), 1275 (1*), 1304 (2), 1332 (1*), 1343 (4*), 1354 (4*), 1443 (8**), 1452 (8**), 1464 (3**), 1476 (1**), 2665 (3 sh, band), 2853 (6*), 2863 (6*), 2899 (3*), 2912 (3*), 2930 (10*), 2941 (10*), 2954 (3*), 2999 (4**), 3014 (4**), 3390–3570 (5; band with a set of frequencies on it).

(II) cis-threo-(2-methyl-1-oxycyclohexyl)-ethylene oxide, $\Delta\nu$ cm^{-1}: 180 (2*)

189 (3*), 206 (2*), 264 (1**), 270(0**), 287 (3), 309 (1), 321 (1*), 331 (3*), 371 (1), 383 (4*), 394 (4*), 411 (0), 455 (5), 486 (6), 509 (1), 527 (2*), 539 (2*), 549 (6* dv), 564 (0), 586 (5 dv), 702 (8 dv), 713 (3 dv), 788 (8), 822 (5), 837 (6), 861 (6), 877 (4), 893 (4*), 904 (3*), 950 (5**), 961 (3**), 978 (6*), 992 (2*), 1005 (6*dv), 1059 (3**), 1084 (5**), 1119 (1*), 1133 (6*), 1144 (0), 1159 (6), 1181 (3 dv), 1232 (2), 1252 (2*dv), 1265 (9*sh, dv), 1275 (2*), 1307 (2), 1332 (1*), 1342 (4*), 1353 (4*), 1443 (8**), 1451 (8**), 1465 (3**), 1479 (1**), 2663 (3sh, band), 2853 (6*), 2863 (6*), 2902 (3*), 2915 (3*), 2929 (10*), 2943 (10*), 2955 (3*), 2991 (4**), 3011 (4**), 3390–3520; 3520–3565 (5; bands adjacent to one another).

(III) trans-erythro-(2-methyl-1-oxycyclohexyl)-ethylene oxide, $\Delta\nu$ cm^{-1}:
183 (2), 189 (0), 203 (2), 230 (0), 263 (2 dv), 286 (1), 296 (3*), 306 (3*), 325 (0), 350 (3*), 358 (3*), 440 (6**), 448 (6**), 461 (3**), 485 (0), 569 (1), 582 (5), 597 (2), 609 (2*), 615 (0*), 634 (0), 680 (0), 700 (1 dv), 718 (7 dv), 777 (2*), 796 (5*), 833 (6), 865 (6*), 878 (2*), 892 (1*), 964 (4), 980 (1*), 993 (1*), 1004 (1*), 1051 (2**), 1066 (4**), 1078 (2**), 1108 (2), 1134 (4), 1157 (4), 1183 (6*), 1213 (6*), 1229 (1), 1252 (7 dv), 1268 (1 dv), 1274 (1), 1298 (0), 1311 (0), 1326 (0*), 1342 (2*), 1361 (1*), 1441 (6**), 1453 (5**), 1463 (3**), 1479 (2**), 2665 (3 sh, band), 2849 (6*), 2868 (6*), 2904 (3*), 2921 (3*), 2928 (10*), 2941 (10*), 2952 (3*), 2991 (3**), 3009 (3**), 3390–3590 (5; band with a set of frequencies on it).

(IV) trans-threo-(2-methyl-1-oxycyclohexyl)-ethylene oxide, $\Delta\nu$ cm^{-1}:
182 (2), 191 (0), 203 (1), 229 (0), 266 (3 dv), 286 (1), 296 (4*), 306 (4*), 320 (0), 349 (4*), 359 (4*), 440 (6**), 448 (6**), 463 (5), 487 (0), 566 (0), 579 (5), 593 (0), 607 (4*), 616 (4*), 634 (0), 681 (0), 703 (1 dv), 716 (8 dv), 794 (6), 835 (6), 861 (4), 885 (4*), 896 (2*), 957 (4), 981 (0*), 990 (5*), 998 (5*), 1056 (3**), 1068 (5r**), 1081 (3**), 1120 (5*), 1136 (2*), 1154 (5*), 1187 (6), 1229 (4), 1252 (1dv), 1269 (6dv), 1275 (3), 1306 (0), 1330 (0*), 1344 (3*), 1357 (2*), 1436 (5**), 1449 (6**), 1465 (3**), 1478 (2**), 2663 (3sh, band), 2852 (6*), 2860 (6*), 2904 (4*), 2917 (3*), 2927 (10*), 2940 (10*), 2954 (3*), 2996 (4**), 3007 (4**), 3520–3565 (5; band, with a weak shoulder adjacent to it on the low-frequency side).

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Note: Figure translations are in progress. See original paper for figures.