Reports and Letters

Relabeling of Cis and Trans Isomers of 1,3-Dimethylcyclopentane

Evidence pointing to the necessity of relabeling the *cis* and *trans* isomers of 1,3-dimethylcyclopentane has recently been presented (*1, 2*). The findings may be summarized as follows.

1) Birch and Dean (*1*) prepared an optically inactive *cis* form of 1,3-dimethylcyclopentane through reduction of *cis*-cyclopentane-1,3-dicarboxylic acid that was obtained by oxidation of bicyclo-[2.2.1]-2-heptene (*3*). This *cis* isomer boiled at the same temperature as, and had physical properties similar to those of, the compound presently designated as the *trans* isomer of 1,3-dimethylcyclopentane (*4*). Employing the method of Pospischill (*5*), Birch and Dean isomerized *cis*-cyclopentane-1,3-dicarboxylic acid to the racemic *trans*-acid with hydrochloric acid. After purification, the racemic *trans*-acid was resolved into *d* and *l* forms that had optical rotations, for the D line of sodium at 15°C, of +21.3° and –22.6°, respectively. The corresponding *trans* isomers of 1,3-dimethylcyclopentane derived from them were optically active and had higher boiling points, higher densities, and higher refractive indices than those of the *cis* isomer. A direct comparison of infrared spectra made by Birch and Dean further confirmed the identity of the two geometric isomers and established that the isomer hitherto designated as *trans* is actually *cis*.

2) On the basis of consideration of the relative energies of the two molecules, Haresnape (*2*) concluded that the *trans* isomer has a greater energy. It is assumed (*6*) that any chain of four carbon atoms with tetrahedral bond angles has a minimum energy when the atoms lie in a planar, zigzag configuration. Any departure from this arrangement can be regarded as a rotation about the central C—C bond. The departure increases the energy of the molecule by an amount that measures the strain energy of rotation. The molecular structure of the cyclopentane ring (*7*) is believed to be one in which four carbon atoms are nearly in a plane and the fifth is displaced above or below this plane. This puckering is regarded as rotating around the ring. Following Beckett, Pitzer, and Spitzer (*6*), and ignoring combinations of carbon atoms involving the ring only, which are identical in the two cases, Haresnape (*2*) considered the average molecule of the *cis* isomer as containing four chains of four carbon atoms distorted by 30° from the planar zigzag configuration and the average molecule of the *trans* isomer as containing three chains distorted by 30° and one chain distorted by 90°. Interpolation between the values of strain energy for 0° and 120° given by Beckett, Pitzer and Spitzer (*6*), and for 180° given by Pitzer (*8*), gives values for 30° and 90° of 0.1 and 0.6 kcal/mole, respectively. Thus the difference in energy between the two isomers is calculated as 0.5 kcal/mole, with the *trans* form having the greater energy. This value is in agreement with the experimental value of 0.54 ± 0.24 kcal/mole (*9, 10*), at 25°C, provided that the names *cis* and *trans* are reversed.

Similar studies made by us along the lines of Haresnape show that the molecule of the *trans* form should in fact be represented as containing, on the average, 14/5 or 2.8 chains of four carbon atoms distorted by 30° and 6/5 or 1.2 chains distorted by 90°. This gives 0.6 kcal/mole for the difference in energy between the *trans* and *cis* isomers, which also agrees with the experimental value, provided that the names *cis* and *trans* are reversed.

It is a matter of experimental fact that, among pairs of geometric isomers, the one possessing less steric hindrance has the lower energy content and usually has the lower boiling point, lower density, and lower refractive index. In light of the information given here, it can be concluded that the *cis* and *trans* isomers of 1,3-dimethylcyclopentane should be relabeled.

For these reasons, a change was made on 30 April 1955 in the naming of the *cis* and *trans* isomers of 1,3-dimethylcyclopentane in the tables of physical and thermodynamic properties, and in the catalogs of spectral data issued by the American Petroleum Institute Research Project 44 at Carnegie Institute of Technology. The changes are such that the lower boiling isomer, formerly labeled *trans*, is now labeled *cis*, and the higher boiling isomer, formerly labeled *cis*, is now labeled *trans*.

The following notations will be used in the tables and catalogs of spectral data listing these compounds (*11*): (i) 1,*cis*-3-dimethylcyclopentane (this isomer, formerly labeled *trans*, has the following properties: boiling point at 1 atm, 90.77°C; refractive index, n_D at 25°C, 1.4063; density at 25°C, 0.7402 g/ml.) (ii) 1,*trans*-3-dimethylcyclopentane (this isomer, formerly labeled *cis*, has the following properties: boiling point at 1 atm, 91.72°C; refractive index, n_D at 25°C, 1.4081; density at 25°C, 0.7444 g/ml).

The naming of these compounds follows the new system (*12*). In addition to the foregoing changes in connection with the work of the American Petroleum Institute Research Project 44, corresponding changes have been made in the work of the American Petroleum Institute Research Project 6. Accordingly, the names of the API standard samples and API research samples of the *cis* and *trans* isomers of 1,3-dimethylcyclopentane have been reassigned. The National Bureau of Standards, which also issues these compounds as NBS standard samples, is accepting this notation.

All workers in other laboratories dealing with 1,*cis*-3-dimethylcyclopentane or 1,*trans*-3-dimethylcyclopentane are invited to relabel these two compounds in the manner described. It is also recommended that, whenever either of the two names is written, one or more properties also be recorded for adequate identification apart from the name *cis* or *trans*. This latter step will completely eliminate any confusion that may arise from this relabeling. Similar changes were made several years ago for the *cis* and *trans* isomers of 1,3-dimethylcyclohexane (*13*).

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