A. N. Shchidlowskaya, Corresponding Member of the Academy of Sciences of the USSR Ya. K. Syrkin, Academician I. N. Nazarov, and V. F. Kucherov

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Abstract

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A. N. Shchidlowskaya, Corresponding Member of the Academy of Sciences of the USSR Ya. K. Syrkin, Academician I. N. Nazarov, and V. F. Kucherov

DIPOLE MOMENTS OF ESTERS OF ISOMERIC CYCLOHEXANE-1,2-DICARBOXYLIC ACIDS

It is usually assumed that the most stable conformation is the chair conformation with the maximum number of equatorial substituents. These assumptions have been confirmed chiefly in studies of various cyclic compounds having methyl and hydroxyl groups as substituents.

In this connection it is of interest to study compounds with more polar substituents, for example, methyl esters of dicarboxylic acids synthesized by I. N. Nazarov and V. F. Kucherov ([1], [2]).

In the series of 1,2-disubstituted cyclohexanes, 3 isomers are possible: a cis isomer having an equatorial-axial arrangement of the substituents (e –a), and a trans isomer in the diequatorial (e –e) or diaxial form (a –a).

Table 1

No.	Substance	B.p., °C/mm Hg	P_∞	P_{el}	P_{or}	$\mu \cdot 10^{18}$, D
1	cis dimethyl cyclohexane-1,2-dicarboxylate	110–111/5	170,43	49,26	121,17	2,41
2	trans dimethyl cyclohexane-1,2-dicarboxylate	135–135,5/17	144,54	49,26	95,28	2,14
3	cis dimethyl cyclohexene-1,2-dicarboxylate	114/5	166,76	48,79	117,97	2,38

No.	Substance	B.p., °C/mm Hg	P_∞	P_{el}	P_{or}	$\mu \cdot 10^{18}$, D
4	trans dimethyl cyclohexene-1,2-dicarboxylate	136/18	140,92	48,79	92,13	2,10
5	cis methyl hydrogen cyclohexane-1,2-dicarboxylate	68–69*	105,03	44,65	60,38	1,70
6	trans methyl hydrogen cyclohexane-1,2-dicarboxylate	94–95*	120,48	44,65	75,83	1,91

* Melting point.

In our experiments, the dielectric constant of benzene solutions was measured by a heterodyne method at 25° at concentrations from 0.003 to 0.007 mole fraction of the dissolved substance. The Hedestrand formula was used to calculate the dipole moments.

The electronic polarization was calculated from bond refractions and from experimental data. The two values showed good agreement.

The dipole moments of ten substances—derivatives of cyclohexane and cyclohexene—were measured.

Tables 1 and 2 give, respectively: structural formulas, temperature constants, total polarizations P_∞, electronic polarizations P_{el}, orientation polarizations P_{or}, and dipole moments.

The dipole moment of dimethyl ester of *cis*-cyclohexane-1,2-dicarboxylic acid is 2.41 D, that of the *trans* form 2.14 D. The *cis* form has a moment larger by 0.27 D. The same regularity is observed for the dimethyl esters of cyclohexene-1,2-dicarboxylic acid, where $\mu = 2.38$ D and 2.10 D, and the difference is 0.28.

Comparison of the dipole moments of isomeric derivatives of cyclohexane and cyclohexene showed that the double bond causes only a slight change in the moment, both for the *cis* and for the *trans* form.

The dipole moments of the isomers of monomethyl ester of cyclohexane-1,2-dicarboxylic acid are lower than those of the dimethyl esters. Possibly this is explained by the formation of an intramolecular hydrogen bond between the oxygen of the carbonyl group and the hydrogen of the O–H group.

It is of interest to compare the dipole moments of the isomers of methyl esters of cyclohexanedicarboxylic acid with the dipole moments of esters of unsaturated dicarboxylic acids, for example with the diethyl esters of maleic and fumaric acids. The difference in the radicals of the ester group should not noticeably affect the magnitudes of the moments. Smyth and Walls (3) determined the dipole moments of the diethyl esters of maleic and fumaric acids at 25 and 50°.

No.	Compound	μ at 25°, D	μ at 50°, D
1.	Diethyl ester of maleic acid	2.54	2.56
2.	Diethyl ester of fumaric acid	2.38	2.40
3.	Dimethyl ester of 1,2-cyclohexanedicarboxylic acid–*cis*	2.41	–
4.	The same–*trans*	2.14	–

As is seen from these data, the dipole moment of the ester of maleic acid is greater than the moment of the ester of fumaric acid. This is additional confirmation of the *cis* configuration of compound 3.

Table 2

No.	Substance	B.p., °C/mm Hg	P_∞	P_{el}	P_{or}	$\mu \cdot 10^{18}$, D
1	CH_3–cyclohexene-$(COOCH_3)_2$, *cis*	110–110.5/4	172.83	53.88	118.95	2.39
2	CH_3–cyclohexene-$(COOCH_3)_2$, *cis*	105–105.5/	173.10	53.88	119.22	2.39

No.	Substance	B.p., °C/mm Hg	P_∞	P_{el}	P_{or}	$\mu \cdot 10^{18}$, D
3	CH_3–cyclohexene-$(COOCH_3)_2$, *trans*	111/5	160.53	53.88	106.65	2.26
4	CH_3–cyclohexene-$(COOCH_3)_2$, *trans*	110–110.5/4	157.32	53.88	103.44	2.23

Table 2 gives the moments of molecules which, unlike the compounds considered previously, have an additional methyl group at C_4.

For isomers 1 and 2, identical values of the moments were obtained. This was to be expected, since the moment of the CH_3 group is equal to the moment of the C–H bond. Isomers 3 and 4 have somewhat smaller moments. We note that isomer 4 is the most stable; all the other forms are converted into it.

Tulinskii, DiGiacomo, and Smyth (^{4}), as well as Kozima and coauthors (^{5}) and Bender, Dervin, Flowers, and Goering (^{6}), used, for calculating the content in solutions of the trans compounds of the diequatorial and diaxial digaloid isomers of cyclohexane, the formula for mixtures, assuming that the moment of the diaxial isomer is equal to zero. For substituents of the ester type of cyclohexane-1,2-dicarboxylic acids, containing irregular groups, the moment of the diaxial isomer (a–a) cannot be taken as equal to zero.

To determine the configuration of the isomers of dimethyl esters of cyclohexane-1,2-dicarboxylic acid, calculations of the dipole moments were carried out under the assumption of free rotation of the $COOCH_3$ groups, taking into account their direction as irregular groups with respect to the cyclohexane ring. For the values of the bond moments, the angle of rotation, and the angle of the moment vector of the irregular $COOCH_3$ group, the data of Smyth (^{7}) were used. The calculation was carried out according to the formula:

$$\mu^2 = (\Sigma\mu_i')^2 + \Sigma(\mu_i'')^2,$$

where i denotes the index of a group with moment μ_i. The moments μ_i are resolved into components μ_i'—parallel to the axis of rotation—and μ_i''—perpendicular to this axis. The arrow under the sign of the first sum means that the moments μ_i' are added vectorially

$$\mu_{\substack{e\text{–}a\\ \text{and } e\text{–}e}} = \sqrt{(2 \cdot 1.74 \cos 70^\circ \cdot \cos 35^\circ)^2 + 2 \cdot 1.74^2 \cdot \sin^2 70^\circ} = 2.51 \text{ D}.$$

The moment of the a—a isomer was calculated from the equation

$$\mu_{a-a} = \sqrt{2(1.74 \cdot \sin 70^\circ)^2} = 2.30 \text{ D}.$$

The value 1.74 represents the moment of the $COOCH_3$ group (^{7}). The experimental value of the moment of the cis isomer lies between the calculated values 2.51-2.30 D.

The experimental moment of the trans isomer, equal to 2.14, does not correspond to the calculated value of the moment of the e—e isomer under the condition of free rotation.

We note that the moment of dimethyl terephthalate, equal to 2.2 D (^{9}), indicates only a slight hindrance of free rotation.

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