Absorption of Microwave Radiation by Solutions

Part 2.—Dielectric Relaxation of (*a*) Cyclohexane-1,4-Dione and some Cyclohexane-1,4-Diols and (*b*) Diphenyl and 0,0′-Ditolyl Sulphides, Sulphoxides and Sulphones

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Electric dipole moments and dielectric relaxation times of thirteen compounds have been calculated from measurements made at radio and at microwave frequencies on dilute solutions in benzene, benzene+dioxan and benzene+nujol solutions at 25.0°C. The results are discussed in terms of molecular conformations and relaxation mechanisms.

Dielectric relaxation of polar molecules in solution occurs by (*a*) overall molecular tumbling and (*b*) by internal flexing motions or rotations of polar groups. The latter, when present, normally have the shorter relaxation time and are usually an important factor in determining the unresolved (average) relaxation time for the molecules. It would seem profitable to study this property for selected cyclohexane derivatives and aromatic sulphides, sulphoxides and sulphones.

EXPERIMENTAL

PREPARATION AND PURIFICATION OF COMPOUNDS

The physical measurements were made immediately after the purification of each compound.

Cis AND trans-CYCLOHEXANE-1,4-DIOLS were prepared by the hydrogenation of hydroquinone at 150° and 150 atm pressure.[1] The diacetyl derivatives of the mixed isomers were separated by fractional crystallization and the diols regenerated and recrystallized to constant m.p. (cis isomer, m.p. 106° ; trans, isomer m.p. 141°).

CYCLOHEXANE-1,4-DIONE was obtained by the dropwise addition of an acetone solution of cyclohexane-1,4-diol to CrO_3 in H_2SO_4 at 0-5°. Solvent was removed from the acetone layer and the product recrystallized from methanol to a constant m.p. (78°).

1,4-EPOXYCYCLOHEXANE was made [2] by heating the cis+trans diol mixture with alumina at 240° and the product fractionally distilled (b.p. 120°/760 mm, n_D^{20} 1.447).

(±) Cis,cis,cis-2,5-DIMETHYLCYCLOHEXANE-1,4-DIOL. p-Xylenol was first oxidized to 2,5-dimethyl-p-benzoquinone (m.p. 125°) by peracetic acid,[3] then reduced to 2,5-dimethylhydroquinone (m.p. 214-215°) by Zn and acetic acid, and finally hydrogenated to a mixture of the diol isomers with hydrogen and a platinum oxide catalyst.[4] The isomers were chromatographed on alumina prepared by neutralizing commercial " neutral " alumina. Elution with ether removed a liquid and a yellow solid and then a 19 : 1 ether+methanol mixture was employed. The required isomer was located by its characteristic infra-red absorption at 3479 cm^{-1}. Recrystallization from benzene gave a white solid of m.p. 79°.

(±) Cis,cis,cis-2,5-DI-ISOPROPYLCYCLOHEXANE-1,4-DIOL. 2,5-Di-isopropylquinone (m.p. 170°) was prepared by a modification of Bogolyubskii and Eroklin's method,[5] hydrogenated, and the diol isomers separated as described above. The required isomer had a m.p. 111° and characteristic infra-red absorption at 3490 cm^{-1}.

(±) Cis,cis,cis-2,5-DI-t-BUTYLCYCLOHEXANE-1,4-DIOL was obtained from 2,5-di-t-butylhydroquinone (m.p. 222°) as described above. The required isomer had a m.p. 156° and characteristic infra-red absorption at 3480 cm^{-1}.

DIPHENYL AND O,O′-DITOLYL SULPHIDES, SULPHOXIDES AND SULPHONES were prepared as described previously.[6]

SOLVENTS were purified as described previously.[7]

EXPERIMENTAL MEASUREMENTS

The electric dipole measurements at radio frequencies were made as described previously [8] and the electric permittivities at microwave frequencies obtained as in part 1.[9] Seven solutions were studied for each compound and all measurements were made at 25.0°C.

RESULTS

Table 1 summarizes the polarization data and dipole moments for the cyclohexane derivatives obtained at radio frequency; α, β and γ are respectively the slopes of the

TABLE 1.—POLARIZATION DATA AND DIPOLE MOMENTS OF CYCLOHEXANE DERIVATIVES AT 25.0°

compound	solvent [a]	max. weight fraction × 10^5	α	β	γ	P_2 (cm^3)	R_D (cm^3)	μ (D)
cyclohexane-1,4-dione	B	2165	1.63_8	−0.310	−0.020	62.42	26.99	1.29
	1 : 2 B/N	994	1.61_0	−0.316		61.33		1.30
1,4-epoxycyclohexane	B	2075	3.17_0	−0.133	−0.141	88 08	26.48	1.74
	1 : 2 B/N	1044	3.11_1	−0.065		89.19		1.75
trans-cyclohexane-1,4-diol	D	1881	5.42_6	−0.056	0.214	134.38	31.48	2.24
	1 : 3 B/D	618	4.83_1	−0 090		126.77		2.16
	3 : 2 B/D	399	4.36_4	−0.168		121.34		2 10
	B[b]							(2.08)
cis-cyclohexane-1,4-diol	D	1889	6.97_1	−0.065	0.214	163.62	31.21	2.55
	1 : 1 B/D	884	6.15_3	−0.174		155.88		2.47
	3 : 1 B/D	685	5.79_2	−0.211		152.84		2.44
	B[b]							(2.42)
cis,cis,cis dimethyl cyclohexane-1,4-diol	B	1563	5.12_0	−0.189	−0.061	179.84	38.69	2.62
cis,cis,cis di-isopropyl cyclohexane-1,4-diol	B	808	5.21_6	−0.119	−0.088	257.61	56.86	3.14
cis,cis,cis di-t-butyl cyclohexane-1,4-diol	B	700	4.69_3	−0.112	−0.098	271.72	64.86	3.14

[a] benzene (B), dioxan (D), nujol (N); [b] extrapolated value for 100 % benzene.

TABLE 2.—ELECTRIC DIPOLE MOMENTS AND RELAXATION TIMES OF CYCLOHEXANE DERIVATIVES AT 25.0°

compound	solvent [a]	frequency × 10^{-12} (s)	max. weight fraction × 10^5	α'	α''	μ (D)	τ × 10^{12} s	τ_t × 10^{12} s	τ_g × 10 s
cyclohexane-1,4-dione	B	9.85	1387	1.576	0 056	1.28	0.57	16	
	B	25.24	9852	1.656	0.191	1.32	0.71		
	1 : 2 B/N	9.86	968	1.519	0.106	1.26	1.1	110	
1,4-epoxycyclohexane	B	9.86	1445	2.783	0.808	1.69	4.5	14	
	B	25.09	2083	1.793	1.451	1.65	4.7		
	1 : 2 B/N	9.86	1132	2.531	1.057	1.70	6.4	98	
trans-cyclohexane-1,4-diol	D	9.86	410	4.350	1.935	2 20	7.5		
	1 : 3 B/D	9.86	435	4.511	1.929	2 26	6.9		
	3 : 2 B/D	9.86	375	3.536	1.767	2.11	8.1		
	B[b]						(7 5)	21[c]	4
cis-cyclohexane-1,4-diol	D	9.86	410	5.200	1.941	2.35	6.1		
	1 : 1 B/D	9.86	444	5.097	2.054	2.42	6.6		
	3 : 1 B/D	9.86	467	4.948	1.614	2.37	5.5		
	B[b]						(6.1)	18[c]	1.4
cis,cis,cis dimethyl-cyclohexane-1,4-diol	B	9.86	1418	3.526	1.419	2.35	6.3	20[c]	1.1
	B	25.20	1576	2.368	1.998	2.33	5.2	26[d]	
cis,cis,cis di-isopropyl-cyclohexane-1,4-diol	B	9.86	824	1.953	1.726	2.54	13.5	32[d]	3.3
	B	25.19	1690	0.706	1.114	2.18	(9.5)		
cis,cis,cis di-t-butyl-cyclohexane-1,4-diol	B	9.86	1356	1.620	1.326	2.40	12.5	32[d]	3.3
	B	24.94	1356	1.233	0.606	1.85	—		

[a] benzene (B), dioxan (D), nujol (N); [b] average value for benzene, dioxan mixed solvents; [c] chair conformation; [d] flexible boat conformation.

graphs of electric permittivities, specific volumes and refractive indices squared against weight fraction. The other symbols have their usual meanings.[8]

Tables 2 and 3 contain the slopes, against weight fraction, of the real (α') and imaginary (α'') parts of the electric permittivity at microwave frequencies, together with the dipole moments μ and relaxation times τ selected as the most likely values from the various calculation procedures detailed in part 1. Because of the low solubility of the cyclohexane-1,4-diols they were only investigated at X-band frequency.

DISCUSSION

CYCLOHEXANE-1,4-DIONE AND SOME CYCLOHEXANE-1,4-DIOLS

The predominant form of cyclohexane derivatives is the chair conformation with as few substituents in axial positions as possible.[10] However, cases have been reported [4, 11] in which the preferred conformation is a modified boat structure called the " flexible form ".

CYCLOHEXANE-1,4-DIONE and 1,4-EPOXYCYCLOHEXANE. The dione has an apparent dipole moment of about 1.3 D. Infra-red and Raman spectroscopic studies [12, 13] demonstrate that the molecules do not possess a centre of symmetry, thus precluding the chair form. The molecule apparently exists predominantly in the flexible conformation (fig. 1) and Allinger [12] has calculated that this is consistent with its dipole moment.

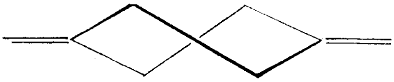

FIG. 1.—Flexible conformation of cyclohexane-1,4-dione.

Accepting that the molecule is polar the literature reports [14] of " negligible electrical loss in xylene and a loss tangent (tan δ) of only 2.2×10^{-3} in benzene " seem surprising. These findings may be due to the measurements being made at too low a frequency, placing ε'' too far from the critical frequency where it is a maximum. As can be seen from table 2 we obtained a relaxation time of 0.7×10^{-12} s in benzene and this is only raised to 1.1×10^{-12} s in a benzene+nujol mixture with a viscosity 6.75 times greater. These are maximum values since if, as is probable, cyclohexane-1,4-dione has a high atom polarization an allowance for this feature would reduce the calculated values for both μ and τ. The low τ values, and relative insensitivity to viscosity, indicates that τ is primarily determined by some internal flexing motion rather than by overall molecular tumbling.

1,4-Epoxycyclohexane is a rigid molecule of similar size to the dione but it can only relax by overall molecular tumbling. Molecular models reveal that the molecule is nearly spherical so its relatively low relaxation time and lack of sensitivity to the viscosity of the medium could be because the effective microscopic viscosity opposing the tumbling motion is far less than the measured macroscopic viscosity of the medium.

cis and trans CYCLOHEXANE-1,4-DIOLS. Kuhn [15] found no evidence for transannular hydrogen bonding in unsubstituted cyclohexane-1,4-diols. The dipole moments of both isomers in benzene solution have been determined by Svirbely and Lander,[16] who found values of 1.8 D (trans) and 2.5 D (cis), but the high temperature of 46° (benzene solvent) and low maximum weight fractions of less than 0.001 and 0.002 respectively cannot have contributed to the accuracy of the results. We preferred to employ benzene+dioxane mixtures as solvents and to extrapolate the results to give a value for 100 % benzene; this was a reliable procedure with other solutes.

The Eyring formula [17] was employed to estimate their dipole moments assuming that they existed in chair conformations with free rotation of each hydroxyl group about its C—O bond. Taking the H—O and C—O bond moments as 1.51 and 1.14 D respectively and 110° bond angles, the predicted results, μ (trans) = 2.44 D and μ (cis) = 2.02 D, are in excellent agreement with the experimental values of 2.42 and 2.06 D respectively. These compounds would experience slight interactions with hydrogen atoms when their hydroxyls are in axial positions but not when they are in the more favoured equatorial positions. Steric hindrance to solvation by dioxan should be more pronounced in both the chair and the flexible forms of cis-cyclohexane-1,4-diol than in the diequatorial chair form of the trans isomer; this is in agreement with the experimental results (table 1) for the rate of change of dipole moment with dioxan content of the solvent. Because of the greater experimental error in measuring relaxation times the values in benzene solutions (table 2) are assumed to be the average for the benzene + dioxan mixed solvents studied.

If a molecule is perfectly rigid relaxation occurs by molecular tumbling and its relaxation time τ_t can be estimated. Fischer [18] modified Debye's original equation, on the basis of a theory by Perrin, to obtain

$$\tau_t = 4\pi\eta fabc/kT$$

where a, b and c are the lengths of the semi-axes of the ellipsoid used to represent the polar molecule, and f is a molecular structure factor whose values have been given by Budo, Fischer and Mizamoto.[19] The viscosity η is the microscopic viscosity and we adopt Fischer's suggestion [20] that it is 0.23 times the macroscopic solvent viscosity; this is a big assumption. Having estimated the relaxation time τ_t for molecular tumbling, that due to the rotation of polar groups within the molecule τ_g can then be estimated from Budo's expression [21] for the resultant, effective, measured relaxation time τ, *provided* the absorption is of the Debye type and is measured at an appreciable distance from the individual frequencies.

The equations have been applied to the rotating hydroxyl groups in cyclohexane-1,4-diols, assuming chair conformations and the same τ value for each hydroxyl group, with the results shown in table 2. The experimental relaxation time and that calculated for molecular tumbling is greater for the trans isomer. Its estimated group relaxation time τ_g of 4×10^{-12} s is acceptable for a slightly hindered rotating hydroxyl group.[22] The lower group relaxation time for the cis isomer suggests an overestimate of τ_t; molecular models indicate that τ_t would be lower for the flexible form.

2,5-DIALKYLCYCLOHEXANE-1,4-DIOLS. Infra-red intensity measurements [4] provide convincing evidence for trans-annular hydrogen bonding in non-chair conformations for cis,cis,cis isomers of 2,5-dialkylcyclohexane-1,4-diols. The estimated non-chair population ranges from 98 % for the di-t-butyl derivative to only 5 % for the dimethyl compound.

Both the di-isopropyl and the di-t-butyl derivatives exist predominantly in the flexible form [4] and both have an estimated group relaxation time of 3.3×10^{-12} s. This is about the value characteristic of free rotation of a hydroxyl group.[22] Independent rotation of each hydroxyl in these hydrogen bonded molecules would not be expected, however, so that a higher value for τ_g was expected; that it was not observed probably reflects the inadequacy of the mathematical treatment.

The dipole moment of cis,cis,cis-2,5-dimethylcyclohexane-1,4-diol (2.63 D) is 0.19 D greater than calculated for the chair conformation by the Eyring formula assuming free rotation of the hydroxyl groups. This could be accounted for by the presence of some hydrogen bonded flexible form with the higher dipole moment (3.14 D) found for the di-isopropyl and di-t-butyl compounds. Its smaller relaxation times are consistent with greatly reduced trans-annular hydrogen bonding.

The experimental dipole moments of the three dialkylcyclohexane-1,4-diols are 0.3-0.6 D higher at radio than at microwave frequencies. This is reproducible and not concentration dependent.

DIPHENYL AND O,O′-DITOLYL SULPHIDES, SULPHOXIDES, AND SULPHONES

Diphenyl ether has an exceptionally low relaxation time (4×10^{-12} s) and one which is relatively insensitive to the viscosity of its solvent medium.[23] At least five explanations [24] have been offered for the origin of the internal relaxation mechanism which must be present, including one involving a mesomeric charge shift acompanying rotation about the C—O bonds. If an analogous mesomeric effect is important in determining the relaxation of diphenyl sulphide formation of its sulphoxide and sulphone would inhibit participation of the lone-pair electrons on the sulphur atom and increase the relaxation time.

From the results (table 3) it will be observed that diphenyl and o,o′-ditolyl sulphides have nearly the same relaxation times. Any internal coupled rotations must be unimpeded by the ortho methyl groups which is as expected from the conformations suggested earlier for these molecules.[6] The relaxation times, 8-9 $\times 10^{-12}$ s, are about twice the value for diphenyl ether implying a smaller contribution from internal rotation; the small increase in molecular size and in dipole moment are unlikely to have this effect.

TABLE 3.—ELECTRIC DIPOLE MOMENTS AND RELAXATION TIMES OF SULPHUR COMPOUNDS AT 25.0°

compound	frequency $\times 10^{-12}$ (s)	max. weight fraction $\times 10^5$	α'	α''	μ (D)	μ (D) radio frequency[6]	$\tau \times 10^{12}$ (s)	τ_t
diphenyl sulphide	9.86	1396	1.360	0.552	1.50	1.55	8.7[a]	40
	25.26	1394	0.898	0.628	1.48		7.0	
diphenyl sulphoxide	9.86	495	4.689	3.878	3.81	4.07	14.5	46
	25.27	558	1.638	3.150	4.06		14.9	
diphenyl sulphone	9 88	96	4.360	5.590	4.85	5.05	24.8[b]	46
	25.26	423	1.505	3.703	5.00		19.0	
o,o′-ditolyl sulphide	25.10	10 256	0.469	0.219	0.94	1.18	8.4	48
o,o′-ditolyl sulphoxide	9.86	482	2.462	3.186	3.85	3.96	22 6	50
	25.09	1731	0 967	1.672	3.47		19.8	
o,o′-ditolyl sulphone	9 85	200	3.207	3 820	4.30	4.91	21.9	50
	25.13	1415	0.876	2.073	4.03		19.7	

literature values: (*a*) 7.2,[2] 9.2,[16] 10.0 [17]; (*b*) 23.2.[16]

In diphenyl sulphoxide the relaxation time is greater but is still low for a molecule of its size and dipole moment showing that the internal relaxation mechanism is still important. In the corresponding o,o′-ditolyl sulphoxide τ is significantly greater which again is consistent with the previously suggested conformation [6] in which steric interaction between the methyl groups and phenyl rings impedes any coupled internal rotation. Both sulphones, in spite of a further increase in μ, have this same larger relaxation time which is lower than calculated for molecular tumbling. Perhaps the 3*d* orbitals of the sulphur atoms, contracted in size by the electronegative oxygen atom, permit some mesomeric relaxation effect with the π-electrons of the phenyl rings; some evidence for this mesomerism is provided by electric dipole moment measurements [6] and ultra-violet absorption frequencies.[25]

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