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A Remark on the Dipole Moment of Cyclohexane-1,4-dione in Relation to Its Flexible Molecular Conformation

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A critical remark on the interpretation of the polarity of cyclohexane-1,4-dione molecule has been made taking into consideration a possible contribution of atomic polarization estimated from the electric permittivity of the compound in the solid state. The value 9.6 cc has been assigned as the minimum for atomic polarization which gives dipole moments, 1.16D (28.6°C), 1.20D (42.9°C), and 1.22D (60.8°C) obtained in benzene solutions. A theoretical calculation of the dipole moment has been made also with an assumed potential barrier of the form, $V(\theta)=V_0\cdot[(\pi-\theta)-2\beta]/2\alpha$, in relation to a flexing intramolecular movement of the molecule, where θ is the angle between two carbonyl groups substituted at the opposite sites of the molecule, V_0 is the potential for a boat form A (with two carbonyl groups at the bow and the stern), and α, β are constants to be determined by applying boundary conditions: $V(\theta)=0$ for $\theta=180°-137°$, and $V(91°)=V_0$. By taking 2.46D as the bond moment of carbonyl group, the best fit has been realized between the theoretical and experimental dipole moments when V_0 is assumed to be close to 6000 cal/mol, *i. e.*, twice as large as the hindering potential for the internal rotation of ethane molecule. Mention has also been made of the mechanism of dielectric absorption by this molecule in benzene solution with particular reference to the flexing motion suggested above.

X-ray crystal analyses of cyclohexane-1,4-dione by Mossel and Romers[1] and by Groth and Hassel[2] have revealed very clearly that the molecule exists as a twisted-boat conformation in the crystal. This is of particular interest in view of the peculiar dielectric behavior of the substance which has long been a subject of controversy. Fairly large values of dipole moment, 1.3—1.6 Debye,[3-9] have been obtained by a number

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[1] A. Mossel and C. Romers, *Acta Crystallogr.*, **17**, 1217 (1964).

[2] P. Groth and O. Hassel, *Acta Chem. Scand.*, **18**, 923 (1964).

[3] O. Hassel and E. Naeshagen, *Tids. Kjemi Bergvesen*, **10**, 81 (1930).

[4] a) C. G. Le Fèvre and R. J. W. Le Fèvre, *J. Chem. Soc.*, **1935**, 1696; b) *ibid.*, **1956**, 3549.

[5] S. Mizushima, "Structure of Molecules and Internal Rotation," Academic Press, New York (1950), p. 176.

[6] Takehiko Chiba and Yonezo Morino, private Communication.

[7] M. Rogers and J. M. Canon, *J. Phys. Chem.*, **65**, 1417 (1961).

of investigators both in solution and in gaseous state, in spite of the presumed nonpolar conformation of the molecule (chair form), while microwave measurement with benzene solutions[10] suggests a smaller dipole moment of ~0.4 Debye, dielectric loss of the solution being far less than the value which might be expected for a normal polar molecule with dipole moment of 1.3—1.6 Debye. An attempt to solve this problem by measuring the Kerr constant has proved to be unsatisfactory.[11,12]

The flexible conformation of cyclohexane-1,4-dione molecule, as revealed by X-ray analyses,[1,2] might explain the apparent dipole moment of the molecule when it is compared with the calculated values of the moment, assuming that the polarity of the molecule is due to a libration of the two polar moieties of the molecule in some range of angles,[8] or to a fixed polar form in which two carbonyl groups substituted at the opposite sites of the molecule make an angle of 155° between each other.[1]

However, we must not forget that most experimental values in literature have been deduced either neglecting the contribution of atomic polarization or assigning to it a small fraction of electronic polarization (5 to 10 percent); an appreciable contribution from atomic polarization should be considered with a flexible molecule such as cyclohexane-1,4-dione. In this respect, the conclusions of some authors[1,8] seem to be misleading.

Recently Cumper *et al.*[13] reported on the microwave measurement of the dipole moment as well as the relaxation time of cyclohexane-1,4-dione molecule in solutions. They refer to very small values of relaxation time ($\tau=0.57-0.71\times10^{-12}$ sec in benzene solutions) compared with observed dipole moment values, $\mu=1.28-1.32$ D, thereby suggesting some internal flexing motion concerning the dielectric absorption by the molecule. Attention should be paid to the fact that they neglect a possible large contribution of atomic polarization throughout their procedure to calculate μ and τ, and that their quotation of the present author's previous work[10] on the microwave absorption of this compound is somewhat erroneous.

It is appropriate, therefore, to make a critical remark on the interpretation of the polarity of the cyclohexane-1,4-dione molecule with particular reference to our recent work[14] on the estimation of atomic polarization by measuring the electric permittivity of this substance in the solid state.

Experimental

Material. Cyclohexane-1,4-dione was synthesized according to the procedure reported by Vincent *et al.*[15] and recrystallized from ethanol followed by vacuum sublimation, then purified through zone-refining: mp=78.5°C.

Apparatus. Measurement of electric permittivity of the compound in the solid state was performed with the use of a twin-T bridge,[16] (1—150 MHz), the sample being set as a compressed disc of 20 mm diameter and 2.42 mm in thickness. Measurement of the dipole moment in benzene solutions was made using a heterodyne, double-beat electric permittivity measuring equipment constructed in our laboratory (1 MHz), with a sample condenser of Sayce-Briscoe type. Details of these methods were reported before.[14]

Results

Electric Permittivity in the Solid State. Results of the measurement of electric permittivity of cyclohexane-1,4-dione in the solid state are shown in Fig. 1 as a function of temperature. Typical values of ε at 3 MHz are: $\varepsilon=3.10$ (35.0°C), 3.13 (45.0°C), 3.57 (55.0°C), 3.57 (65.0°C), 4.01 (72.0°C).

No appreciable dispersion was observed in the frequency and temperature ranges covered. We see that electric permittivity shows a distinct variation at the transition points 48°C and 69°C,[17] suggesting the onset of some molecular motion above the temperatures so as to give rise to the increase of electric permittivity, despite the increase of molar volume by 2.7% on the

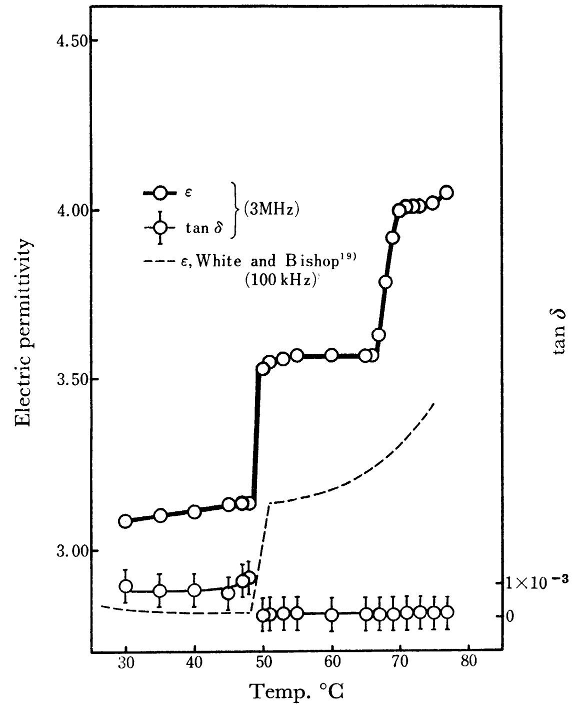

Fig. 1. Electric permittivity of cyclohexane-1,4-dione in the solid state (3 MHz).

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[8] a) N. L. Allinger, *J. Amer. Chem. Soc.*, **81**, 5727 (1959); b) N. L. Allinger and L. A. Freiberg, *ibid.*, **83**, 5028 (1961); c) N. L. Allinger, H. M. Blatter, L. A. Freiberg, and F. M. Karkowski, *ibid.*, **88**, 2999 (1966).

[9] A. Aihara, K. Chitoku, and K. Higasi, unpublished data.

[10] A. Aihara, K. Chitoku, and K. Higasi, This Bulletin, **35**, 2057 (1962).

[11] C. G. Le Fèvre and R. J. W. Le Fèvre, *Rev. Pure and Appl. Chem.*, **5**, 261 (1955).

[12] C. Y. Chen and R. J. W. Le Fèvre, *Australian J. Chem.*, **16**, 917 (1963).

[13] a) C. W. N. Cumper, A. Melnikoff, and R. F. Rossiter, *Trans. Faraday Soc.*, **65**, 2892 (1969); b) C. W. N. Cumper and R. F. Rossiter, *ibid.*, **65**, 2900 (1969).

[14] C. Kitazawa and A. Aihara, *Nippon Kagaku Zasshi*, **90**, 365 (1969).

[15] J. R. Vincent, A. F. Thompson, Jr., and L. I. Smith, *J. Org. Chem.*, **3**, 603 (1939).

[16] Fujisoku dielectrometer type 3.

[17] A. Aihara, T. Chiba, and M. Kawano, *Nippon Kagaku Zasshi*, **86**, 708 (1965).

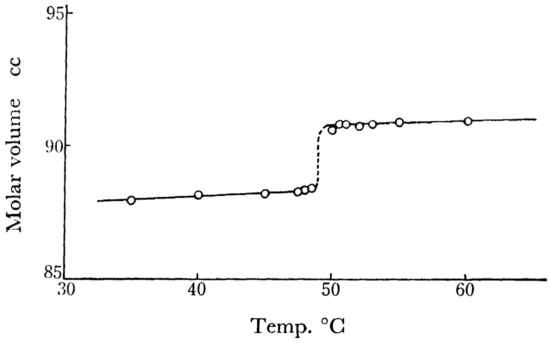

Fig. 2. Variation of the molar volume of cycloane-1,4-dione with temperature.

phase transition at 48°C (Fig. 2).

On the other hand there is a slight decrease in loss tangent (from tan $\delta=1\times10^{-3}$ to ~0) at 48°C when the solid undergoes a transition from the low-temperature phase to the high-temperature one. This is in remarkable contrast with the abrupt increase in electric permittivity at this temperature.

The above fact is of importance in considering the mechanism of the phase transition of this compound,[14] although rather large experimental errors ($\pm0.5\times10^{-4}$ in tan δ) prevent us from making any precise argument. It should be added here that Smyth[18] ascribed this transition to "half rotation" of the molecule referring to the experimental results by White and Bishop.[19] The variation of electric permittivity at 69°C is also remarkable, but no detectable changes were observed in tan δ.

Estimation of the Magnitude of Atomic Polarization. By assuming that the molecules of cyclohexane-1,4-dione are almost rigid at the crystalline lattice at temperatures below 48°C,[1,17] the molar distortion polarization may be calculated from the Clausius-Mossotti equation. With electric permittivity $\varepsilon=3.13$ and molar volume=88.22 cc (density=1.271) both at 45°C, distortion polarization P_D has been found to be 36.6 cc. Subtracting electronic polarization $P_E=27.01$ cc[20] from P_D, 9.6 cc can be assigned as the probable minimum value for the contribution of atomic polarization P_A. This value has been taken into consideration in calculating the dipole moment as measured in benzene solutions.

Dipole Moment in Benzene Solution. Electric permittivity and density as well as refractive index of cyclohexane-1,4-dione in benzene solutions were measured in the concentration range 2.67×10^{-3}—2.49×10^{-2} (weight fraction) and at temperatures 28.6—60.8°C. The values of dipole moment were then calculated from the equations and methods of Halverstadt and Kumler[21] and of Guggenheim and Smith.[22] In Table 1, the values calculated both with and without due consideration of atomic polarization (9.6 cc) are shown. It should be noted that the μ values calculated neglecting P_A (Halverstadt-Kumlers' method) are in good agreement with those calculated by the Guggenheim-Smith equation. These values both correspond to the values in literatures.[3-9]

TABLE 1. DIPOLE MOMENT OF CYCLOHEXANE-1,4-DIONE IN BENZENE SOLUTION (Debye)*

Temp. °C	μ_{H-K} ($P_A=9.6$ cc)	μ_{H-K} ($P_A=0$ cc)	μ_{G-S}
28.6	1.16	1.35	1.33
35.6	1.17	1.36	1.35
42.9	1.20	1.39	1.36
51.1	1.21	1.40	1.39
60.8	1.22	1.42	1.40

* Experimental errors in μ's are estimated to be±0.20 D. μ_{H-K} and μ_{G-S} refer to the dipole moment according to Halverstadt-Kumlers' and Guggenheim-Smiths' methods, respectively.

Discussion

The values of dipole moment, obtained with due consideration of atomic polarization, $P_A=9.6$ cc, should be regarded as the maximum value of the experimental dipole moment, since we might expect a still greater contribution of atomic polarization for the molecule, in solution or in vapor phase, because of its large flexibility. For example, 14.9 cc can be obtained as P_A value if we use $\varepsilon=3.57$ and molar volume=90.94 cc both at 55°C, for the phase above 48°C, where the freedom of motion of the molecule is thought to be much larger as revealed by IR and NMR measurements.[17]

The flexing motion of the molecule could produce a very large increment of electric polarization making the distinction between atomic and orientation polarization ambiguous. Therefore, let us take the dipole moment values calculated with $P_A=9.6$ cc as the most probable experimental values at the moment, and compare them with those calculated theoretically.

Calculation of the Theoretical Dipole Moment and the Geometry of the Molecule. The data of molecular dimensions of cyclohexane-1,4-dione, obtained by Mossel and Romers,[1] differ somewhat from the values usually adopted as normal bond lengths and valency angles: $C(sp^3)-C(sp^2)$ 1.515 Å, $C(sp^3)-C(sp^3)$ 1.536 Å, C=O 1.210 Å, $\angle C(sp^3)C(sp^2)C(sp^3)$ 116.2°, $\angle C(sp^2)C(sp^3)$-$C(sp^3)$ 112.2°.

Therefore it is necessary to estimate anew, with the above data, the angle between the two carbonyl groups substituted at the opposite sites of the molecule for the two conformations, boats A and B (Fig. 3).

A simple geometrical consideration leads to the following values of the angles between the two carbonyl groups for the two boat conformations: $\theta=91.2°$ (boat A), $\theta=136.9°$ (boat B). A comparison is made in Table 2 with the values adopted by Le Fèvre[4] and also by Allinger *et al.*[8c]

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[18] C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill, New York (1955), p. 143.

[19] A. H. White and W. S. Bishop, *J. Amer. Chem. Soc.*, **62**, 8 (1940).

[20] The value was calculated as the sum of the bond electronic polarizations proposed by Le Fèrve and Steel [*Chem. Ind.* (London), **1961**, 670].

[21] I. F. Halverstadt and W. D. Kumler, *J. Amer. Chem. Soc.*, **64**, 2988 (1942).

[22] J. W. Smith, *Trans. Faraday Soc.*, **46**, 394 (1950).

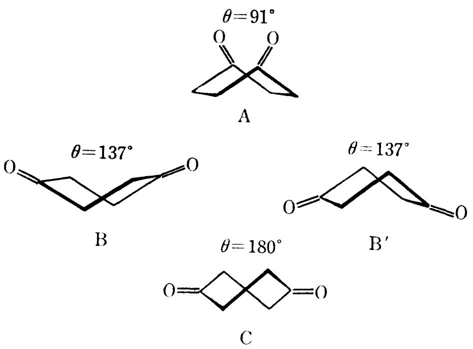

Fig. 3. Boat conformations of cyclohexane-1,4-dione molecule.

TABLE 2. THE ANGLE θ BETWEEN THE TWO CARBONYL GROUPS OF CYCLOHEXANE-1,4-DIONE MOLECULE CALCULATED FOR BOAT FORMS A AND B

	This work	Le Fèvre[4]	Allinger[8c]
Boat A	91.2°	86°	76°
Boat B	136.9°	130°	127°

The angle value observed with the actual molecular conformation in the crystalline state is 154.8°,[1] which means that the molecule is more flattened than boat B. Thus, if this conformation is taken as corresponding to the minimum internal energy even as a free molecule, the dipole moment of the molecule could be calculated with the use of an appropriate value of the C=O bond moment: $\mu=2\ \mu_{\mathrm{C=O}}\times\cos(155°/2)$.

It should be noted, however, that the angle of 155° might not necessarily correspond definitely to the minimum of the potential energy of a free molecule, but could vary within an appreciable range of angles under the influence of external forces, as can be seen from the work by Groth and Hassel,[23] who report the value of 175° as the angle between the two carbonyl groups of cyclohexane-1,4-dione forming a molecular complex with $HgCl_2$, and 157° for the complex with C_2I_2.

An inspection of Dreiding model of this molecule reveals that the relative configuration of the two adjacent methylene groups (mutually gauche) does not change under the deformation of the molecule when the deformation is restricted within the two extreme conformations, boats B and B′, including an intermediate boat C (nonpolar form). The methylene groups do not make any rotation relative to each other so far as the angle between the two carbonyl groups remains within the range 137°—180°. Furthermore, the relative configuration of a carbonyl group to the two adjacent methylene groups varies in such a way as to compensate each other the increase of the potential energy due to deformation. Allinger *et al.*[8c] also discussed the problem.

Thus, admittedly the Dreiding model should not be taken to represent the real molecular structure, we might safely assume that the polar moiety of the molecule "librates" almost freely in a shallow potential well so far as the angle θ does not decrease beyond 137°. If angle θ decreases further, the potential energy of the molecule will increase due presumably to the interaction between the two adjacent methylene groups known in the cases of ethane and its derivatives.[24]

According to the above reasoning, the dipole moment of the molecule can be expressed as follows:

$$\mu^2 = \int_{\theta_1}^{\theta_2} \mu_\theta^2 \exp(-V(\theta)/RT)\mathrm{d}\theta \Big/ \int_{\theta_1}^{\theta_2} \exp(-V(\theta)/RT)\mathrm{d}\theta, \tag{1}$$

where μ_θ is the resultant moment of the molecule corresponding to the angle θ between the two dipole components $\mu_{\mathrm{C=O}}$, the moment of the single carbonyl group, and is given by $\mu^2_\theta=2\ \mu^2_{\mathrm{C=O}}\ (1+\cos\theta)$; $V(\theta)$ is the intramolecular potential as a function of θ, R is the gas constant, T is the absolute temperature and θ_1, θ_2 should be taken as the values for boat C (180°) and boat A (91°),[25] respectively.

It is necessary to make a proper choice of the value for the bond moment $\mu_{\mathrm{C=O}}$ and also of the potential $V(\theta)$ as a function of θ. Allinger *et al.*[8c] took 3.0 D for $\mu_{\mathrm{C=O}}$ and calculated μ values as 1.64 D (291°K) and 1.79 D (490°K), through a graphical integration of Eq. (1) from $\theta_1=76°$ to $\theta_2=180°$, with the assumption that the potential barrier for the boat A conformation is given either by 10.26 kcal/mol (291°K) or 12.00 kcal/mol (490°K). Their μ values are obviously too large compared with the values in literature, and do not give a reasonable explanation of the polarity of this molecule.

The authors have chosen a value 2.46 D for the C=O bond moment. The difference between experimental dipole moment of cyclohexanone, $\mu=2.87$ D, obtained by the measurement of Stark effect on the microwave absorption of the substance,[26] and the moment of methylene group, 0.46 D (the moment of $-CH_3$ is assumed to be 0.40 D), is 2.41 D, while we get $\mu_{\mathrm{C=O}}=2.50$ D if we subtract $\mu_{-\mathrm{CH_3}}=0.40$ D from the experimental dipole moment of acetone, $\mu=2.90$ D.[27] The average of these two values, 2.46 D, may be regarded as free from any contribution of atomic polarization and, therefore, must be more reasonable as the bond dipole moment of C=O for cyclohexane-1,4-dione molecule.

On the other hand, the following assumption has been made concerning the potential function of this molecule. The potential energy is zero for the range of θ values, 137° to 180°, but varies as $V(\theta)=V_0[(\pi-\theta)-2\beta]/2\alpha$ between 91° and 137°, where V_0 is the potential barrier for the conformation A ($\theta=91°$), α and β are constants. Converting the variable θ to $\varphi=(\pi-\theta)/2$, the potential becomes $V(\varphi)=V_0(\varphi-\beta)/\alpha$, (Fig. 4). α and β can be determined by applying the boundary conditions, $V(\varphi)=0$ for $\varphi=21.5°$ and $V(\varphi)=V_0$ for $\varphi=44.5°$.

Then, rewriting Eq. (1) as

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[23] P. Groth and O. Hassel, *Tetrahedron Lett.*, **1964**, 65.

[24] S. Mizushima, *loc. cit.*, Chapters 1—3.

[25] In the case of boat A, the two adjacent methylene groups become mutually "eclipsed," corresponding to the maximum of the intramolecular potential.

[26] Y. Ohnishi and K. Kozima, This Bulletin, **41**, 1323 (1968).

[27] J. W. Swalen and C. C. Costain, *J. Chem. Phys.*, **31**, 1562 (1959).

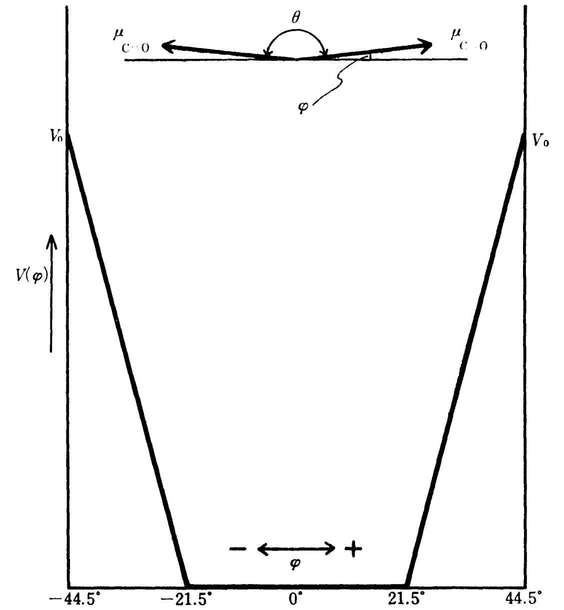

Fig. 4. Assumed potential curve for the flexing motion of cyclohexane-1,4-dione molecule.

$$\mu^2 = 2\mu^2_{C=O}\{1+\langle\cos\,\theta\rangle\}, \qquad (2)$$

the statistical average of cos θ, $<$cos $\theta>$, can be calculated in the following way:

$$\langle\cos\theta\rangle = \int_{0^\circ}^{44.5^\circ} -\cos 2\varphi \exp\{-V(\varphi)/\boldsymbol{R}T\}\mathrm{d}\varphi \Big/ \int_{0^\circ}^{44.5^\circ} \exp\{-V(\varphi)/\boldsymbol{R}T\}\mathrm{d}\varphi$$

$$= -\left[\int_{0^\circ}^{21.5^\circ} \cos 2\varphi \mathrm{d}\varphi + \int_{21.5^\circ}^{44.5^\circ} \cos 2\varphi \exp\{-V_0(\varphi-\beta)/\alpha\boldsymbol{R}T\}\mathrm{d}\varphi\right] \Big/ \left[\int_{0^\circ}^{21.5^\circ} \mathrm{d}\varphi + \int_{21.5^\circ}^{44.5^\circ} \exp\{-V_0(\varphi-\beta)/\alpha\boldsymbol{R}T\}\mathrm{d}\varphi\right] \qquad (3)$$

Integration has been performed analytically for three temperatures (28.6°C, 42.9°C, 60.8°C) with the assumption that the potential barrier V_0 can be taken as 6000 cal/mol: the potential for the boat A conformer may approximately be chosen to be twice as large as the hindering potential barrier for the internal rotation of ethane molecule, 3000 cal/mol.[24)] The results of calculation are shown in Table 3, together with the results obtained by using the potential barrier of $V_0=$ 5000 cal/mol and $V_0=10000$ cal/mol, the latter being of the same order of magnitude as those adopted by Allinger *et al.*[8c)]

TABLE 3. THEORETICAL DIPOLE MOMENT OF CYCLOHEXANE-1,4-DIONE AS COMPARED WITH EXPERIMENTAL VALUES (Debye)

Temp. °C	μ_{calc}			μ_{obs}
	$V_0=5000$ cal/mol	$V_0=6000$ cal/mol	$V_0=10000$ cal/mol	
28.6	1.19	1.17	1.11	1.16±0.02
42.9	1.20	1.18	1.11	1.20±0.02
60.8	1.21	1.19	1.12	1.22±0.02

In spite of a simplified form of the potential function here adopted, the calculated values of dipole moment with $V_0=5000$—6000 cal/mol are in very good agreement with the experimental values with the consideration of atomic polarization. It is, therefore, most probable that the molecule of cyclohexane-1,4-dione behaves, in a solution, as a flexing twisted-boat conformation with the potential for the intramolecular movement of the form as shown in Fig. 4.

With the potential of this form, the molecule will be able to relax quite easily, under the action of high frequency electric field, without being subjected to appreciable hindrance in changing the direction of the molecular dipole. The flexing motion of this molecule could reverse the sense of polarity of the molecule instantaneously without performing rotation of the molecule as a whole, if the angle φ changes from positive to negative values (Figs. 3 and 4). This must be the reason why solutions of cyclohexane-1,4-dione give unexpectedly small dielectric loss[10)] as well as small τ values,[13)] but rather large increment of electric permittivity.[10)]