

### 392. *The Dipole Moments of Some Cyclic Carbonates.*

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The dipole moments and dielectric constants of ethylene carbonate and monochloro-, 1 : 2-dichloro-, methyl-, and chloromethyl-ethylene carbonate have been determined. The possibilities of intermolecular association in these compounds, and the effects of chlorine- and methyl-substitution on the dipole moment of the parent carbonate, are considered.

DURING an investigation of the solvent properties of cyclic esters of carbonic acid, it was found that anhydrous ferric, mercuric, and zinc chlorides were readily soluble in ethylene carbonate. The solutions show a considerable electrical conductivity, indicating that ionisation occurs. By comparison, the alkali-metal chlorides are practically insoluble in ethylene carbonate.

Anomalous properties of cyclic carbonates have been reported. Newman and Addor<sup>1</sup> noted the decrease in boiling-point of ethylene carbonate upon substitution of chlorine for hydrogen. Hales, Jones, and Kynaston,<sup>2</sup> whilst investigating the infrared absorption spectra of cyclic carbonates, observed two absorption peaks in the carbonyl region for monochloro- and 1 : 2-dichloro-ethylene carbonate. An analogous phenomenon, reported for halogenated esters of acetic acid, was ascribed to intermolecular association,<sup>3</sup> as the doublet was not observed in the case of methyl- and chloromethyl-ethylene carbonate, however, Hales, Jones, and Kynaston<sup>2</sup> considered rotational isomerism to be the more likely explanation of their observed effect.

Values of dipole moments of ethylene carbonate and some other cyclic carbonates have been reported;<sup>4,5</sup> all these compounds possess large dipole moments. Longster and Walker<sup>6</sup> investigated the effect of permanent dipoles on the cohesive energy and solvent action towards high polymers of highly polar substances, and in this context pointed out the high boiling-points and cohesive energies of cyclic, as compared with open-chain, carbonates.

The ability to dissolve electrolytes, with formation of electrically-conducting solutions, depends largely upon the dielectric constant of the solvent and this, in turn, partly upon the dipole moment of the solvent molecule. We have determined the dipole moments and dielectric constants of ethylene carbonate and monochloro-, 1 : 2-dichloro-, methyl-, and chloromethyl-ethylene carbonate, and drawn conclusions regarding the possibilities of intermolecular association in the liquids.

<sup>1</sup> Newman and Addor, *J. Amer. Chem. Soc.*, 1953, **75**, 1263.

<sup>2</sup> Hales, Jones, and Kynaston, *J.*, 1957, 618.

<sup>3</sup> McBee and Christman, *J. Amer. Chem. Soc.*, 1955, **77**, 755.

<sup>4</sup> Arbutov and Shavsha, *Doklady Akad. Nauk S.S.S.R.*, 1949, **68**, 1045.

<sup>5</sup> *Idem*, *Chem. Abs.*, 1950, **44**, 886.

<sup>6</sup> Longster and Walker, *Trans. Faraday Soc.*, 1953, **49**, 228.

## EXPERIMENTAL

*Materials.*—Ethylene carbonate was fractionally distilled at reduced pressure, and then fractionally crystallised from dry ether. The purified material had m. p. 36.2°,  $n_D^{40}$  1.4199.

Samples of monochloro-, 1:2-dichloro-, methyl-, and chloromethyl-ethylene carbonate, prepared as in ref. 7, supplied by Dr. J. Idris Jones. These were redistilled in nitrogen at reduced pressure. Their physical properties are given in the Tables.

The benzene for dipole-moment measurements was prepared from "AnalaR" material by Le Fèvre's method;<sup>8</sup> a comparison sample, purified by Rybicka and Wynne-Jones's procedure,<sup>9</sup> showed no difference in physical properties.

TABLE 1. *Properties of cyclic carbonates.*

Substance	$n_D$	$d_4^{25}$	$R_D$	$\epsilon$ *†	$10^{18} \mu$ (e.s.u.)	B. p.
Ethylene carbonate *	1.4199	1.3208	16.93	89.6	4.87	238°
Methylethylene carbonate .....	1.4212	1.2065	21.46	61.7	4.94	232
Monochloroethylene carbonate ...	1.4603	1.5198	22.09	62.0	3.99	212
1:2-Dichloroethylene carbonate...	1.4615	1.5830	27.22	31.8	3.44	178
Chloromethylethylene carbonate...	1.4680	1.4403	26.35	97.5	4.68	252

\* Measurements at 40°.

† The results are the mean of three series of determinations. The experimental error is estimated as  $\pm 0.3\%$ .

TABLE 2. *Total polarisations and dipole moments in benzene.*

Ethylene carbonate							
$\kappa$	$d_4^{25}$	$\epsilon$	$T^P$	$\kappa$	$d_4^{25}$	$\epsilon$	$T^P$
0.0	0.87366	2.2725	—	0.0058225	0.87584	2.4696	493.4
0.0036502	0.87496	2.3955	499.9	0.0079409	0.87662	2.5430	488.4
0.0043616	0.87533	2.4198	497.6				
$P_0 = 510.2$ ; $D^P = 17.8$ ; $\mu = 4.87 \times 10^{-18}$ e.s.u.							
Methylethylene carbonate							
$\kappa$	$d_4^{25}$	$\epsilon$	$T^P$	$\kappa$	$d_4^{25}$	$\epsilon$	$T^P$
0.0032595	0.87480	2.3844	515.8	0.010327	0.87714	2.6223	484.2
0.0056013	0.87566	2.4633	502.8	0.014818	0.87860	2.7639	461.2
$P_0 = 529.0$ ; $D^P = 23.0$ ; $\mu = 4.94 \times 10^{-18}$ e.s.u.							
Monochloroethylene carbonate							
$\kappa$	$d_4^{25}$	$\epsilon$	$T^P$	$\kappa$	$d_4^{25}$	$\epsilon$	$T^P$
0.0034450	0.87575	2.3503	349.1	0.0073910	0.87807	2.4406	344.9
0.0039360	0.87613	2.3615	347.9	0.011994	0.88078	2.5472	339.5
$P_0 = 352.6$ ; $D^P = 23.2$ ; $\mu = 3.99 \times 10^{-18}$ e.s.u.							
1:2-Dichloroethylene carbonate							
$\kappa$	$d_4^{25}$	$\epsilon$	$T^P$	$\kappa$	$d_4^{25}$	$\epsilon$	$T^P$
0.0032137	0.87622	2.3269	273.4	0.0085933	0.88036	2.4194	272.7
0.0053052	0.87784	2.3623	273.2	0.012337	0.88320	2.4858	272.1
$P_0 = 274.0$ ; $D^P = 28.6$ ; $\mu = 3.44 \times 10^{-18}$ e.s.u.							
Chloromethylethylene carbonate							
$\kappa$	$d_4^{25}$	$\epsilon$	$T^P$	$\kappa$	$d_4^{25}$	$\epsilon$	$T^P$
0.0042304	0.87637	2.4041	470.6	0.0082567	0.87877	2.5302	460.4
0.0054554	0.87705	2.4428	468.7	0.010219	0.87998	2.5913	454.6
$P_0 = 481.8$ ; $D^P = 27.7$ ; $\mu = 4.68 \times 10^{-18}$ e.s.u.							

*Dipole Moments.*—Determinations were made in benzene solutions by a resonance method with the apparatus described by Few, Smith, and Witten.<sup>10</sup> The crystal-controlled oscillator frequency was  $10^6$  c./sec., and the capacitance was measured by a Sullivan precision air condenser. The cell was of an all-glass type, similar to that described by Le Fèvre, and had a capacitance of  $65 \mu\mu F$  per dielectric-constant unit.

Densities were determined by a modified Sprengel-Ostwald pycnometer of ca. 20 c.c. capacity, and refractive indices by an Abbé refractometer.

<sup>7</sup> "Chemistry Research," 1953. Department of Scientific and Industrial Research, pp. 37—38; 1954, pp. 35—36.

<sup>8</sup> Le Fèvre, "Dipole Moments," Methuen's Monograph, London, 1948.

<sup>9</sup> Rybicka and Wynne-Jones, *J.*, 1950, 3671.

<sup>10</sup> Few, Smith, and Witten, *Trans. Faraday Soc.*, 1952, **48**, 211.

*Dielectric Constants.*—The above resonance apparatus was used, but with a Hartley-Barrett type of conductivity cell. The distance between the two plane-parallel bright platinum electrodes was adequate to prevent errors due to the fringing effect of capacitance between the adjacent mercury-filled lead-in tubes. This effect was reduced further by always using the same volume of liquid in the cell.

Methanol-water mixtures of known dielectric constant, as determined by Albright and Gosting,<sup>11</sup> were used to calibrate the cell. The measurements were made at 40°, so that it was necessary to calculate dielectric constants at 40° for the calibrating solutions by linear interpolation between 35° and 45°.

*Results.*—The results are summarised in Tables 1 and 2. Molar refractions,  $R_D$ , were derived from densities and refractive indices of the pure compounds at 25°, except for ethylene carbonate (40°).  $P_0$  was obtained by extrapolation to zero concentration of values of  ${}_T P$ , the total polarisation at mole fraction  $x$ . Dipole moments were calculated from  $\mu = 0.01275\sqrt{[(P_0 - {}_D P)T]}$  where the distortion polarisation,  ${}_D P$ , is given by  ${}_D P = P_{\text{atom}} + P_{\text{electron}} = 1.05R_D$ .

#### DISCUSSION

The value obtained for the dipole moment,  $\mu$ , of ethylene carbonate in benzene agrees well with those of Arbuzov and Shavsha<sup>4</sup> (4.80 D) and Longster and Walker<sup>6</sup> (4.60 D). The substitution of hydrogen by a methyl group increases  $\mu$  by 0.07 D; Arbuzov and Shavsha found the same increase between 1:3-propylene carbonate ( $\mu = 5.21$  D) and 1:3-butylene carbonate ( $\mu = 5.28$  D). For 2:3-butylene carbonate an even higher dipole moment ( $\mu = 5.26$  D) was found.<sup>6</sup> This increase of dipole moment on introduction of methyl groups as substituents was generally observed by Baker,<sup>12</sup> and has been extensively investigated. The effect, as seen in Tables 1 and 2, is only slightly reduced by substitution by a monohalogenated methyl group.

Chlorine atoms, directly attached to the ethylene carbonate ring, decrease  $\mu$ ; this is not surprising, for the group moment of the C-Cl linkage is in opposition to the resultant moment of the carbonate group. The same conclusion can be reached for vinylene carbonate. Slayton, Simmons, and Goldstein<sup>13</sup> found  $\mu = 4.51$  D, less than that of ethylene carbonate. The double bond is localised, the characteristic C=O absorption band being unchanged as compared with that of other cyclic carbonates.<sup>2</sup> If the double bond were delocalised, however, a decrease in absorption within this band would be expected. The accumulation of negative charge due to the  $\pi$ -bond causes a moment opposing that of the carbonate group.

The forces between the molecules of a liquid are usually classified as orientation forces, dispersion forces, and inductive forces. The first are particularly important in the case of highly polar molecules, and the last are very small. The dielectric constant of a medium can be regarded as a semi-quantitative resultant of these forces.

The progressive reduction in b. p. and dielectric constant, with replacement of hydrogen by chlorine in ethylene carbonate, reflects mainly the decreasing dipole moment. The orientation forces are presumably weaker, in vinylene carbonate, for here a "normal" b. p. (162°) and high dipole moment are found.

The change from a methylene carbonate to the monochloro-derivative leads to the expected decrease in dipole moment, but there is a small increase in b. p. and a large increase in dielectric constant. It is thought that intermolecular hydrogen bonding may assist dipole interaction in the last case.

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<sup>11</sup> Albright and Gosting, *J. Amer. Chem. Soc.*, 1946, **68**, 1061.

<sup>12</sup> Baker, *J.*, 1939, 1152.

<sup>13</sup> Slayton, Simmons, and Goldstein, *J. Chem. Phys.*, 1954, **22**, 1678.