The Crystal Structure of 1,1,2,2-Tetracarbomethoxyethane. The Conformation of the Carbomethoxy Group

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A study of the crystal structure of dimethyl oxalate showed that the molecule is planar and that the methyl group and the carbonyl oxygen are eclipsed.[1] A comparison of these findings with results obtained in the liquid and vapor phases indicates that the most stable conformation of the ester group is generally the one in which the four atoms constituting the ester function (CO_2C) are nearly coplanar. Furthermore, the alkyl group and the carbonyl oxygen prefer to be eclipsed.[2-6] The dimer of dimethyl malonate, 1,1,2,2-tetracarbomethoxyethane, appeared to be an attractive molecule for further investigation of conformational aspects of the ester group since the ester group in this molecule is contained in an unusual molecular environment.

Crystals of the ester were grown from methanol and were obtained as hard, colorless, thick plates. The crystals selected for mounting were parallelepipeds approximately 0.5 mm wide, 0.5 mm long, and 0.4 mm thick. The X-ray data were collected around three axes using multifilm equi-inclination Weissenberg photographs with Cu Kα radiation at ambient temperatures. The crystals were stable in the X-ray beam and no decomposition was noted during the time required to collect the data. Intensities were measured by comparison of photographs with a calibrated film strip, and 1084 independent reflections were observed. Lorentz and polarization corrections were applied, interlayer scaling corrections were applied, and the data were placed on an absolute scale using Wilson's method.[7] The structure factors were then converted into E values.

The crystal data are as follows: monoclinic, mp 137.5–138.5°; $a = 6.81 \pm 0.02$, $b = 7.60 \pm 0.02$, $c = 12.44 \pm 0.02$ A; $\beta = 107.9° \pm 0.4°$; $V = 612.6$ Å^3. The observed density (by flotation in toluene–carbon tetrachloride solution) was found to be 1.40 g/cc; the calculated value is 1.42 g/cc; $Z = 2$. From extinctions, $h0l$ absent with l odd, $0k0$ absent with k odd, the space group was determined to be $P2_1/c$.

The structure was solved by direct methods using the symbolic addition procedure.[8] Phase determination was routine and the signs of 252 reflections with E values greater than 1.0 were readily determined. An E map based on these data clearly revealed the structure. Refinement was carried out by differential syntheses with anisotropic temperature factors until R had reached a final value of 11.6% for 1084 independent reflections; hydrogen atoms were ignored throughout the calculations. All computations were carried out on an IBM 7072 computer with programs written in Professor G. A. Jeffrey's laboratory at the University of Pittsburgh.

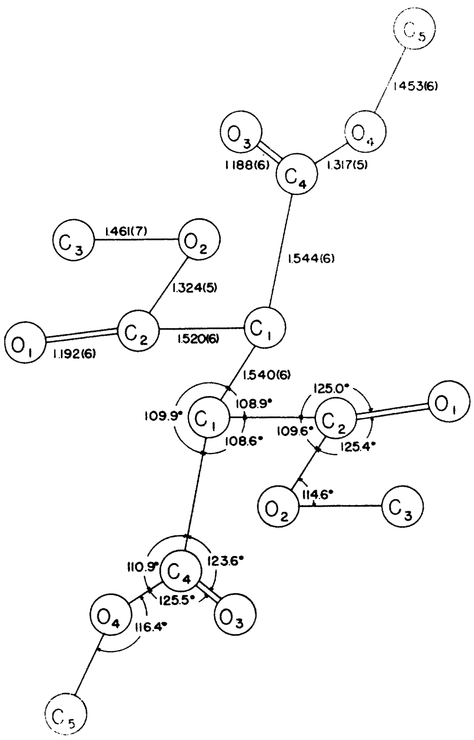

Figure 1.—1,1,2,2-Tetracarbomethoxyethane, [*b*] axis projection.

Results and Discussion

The molecule possesses a center of symmetry and makes use of this while crystallizing in the monoclinic space group, $P2_1/c$. Atomic coordinates with standard deviations are listed in Table I, and anisotropic thermal factors are recorded in Table II. A view of the molecule down the [*b*] axis is shown in Figure 1.

Least squares planes were calculated for each of the five atoms comprising the ester group in terms of orthogonal axes, X, Y, and Z'. The plane through C_1, C_2, C_3, O_1, and O_2 shows that these atoms are distributed in the plane

$$0.9117X + 0.4108Y - 0.0103Z' = 0.1230$$

with deviations of 0.008, −0.002, 0.0011, −0.003, and −0.014 Å, respectively. The five atoms of the second ester group, C_1, C_4, C_5, O_3, and O_5, also form a plane and the constants are

$$-0.5597X + 0.5676Y + 0.6038Z' = -0.3316.$$

The deviations of the atoms from this plane were −0.015, 0.006, −0.020, 0.004, and 0.025 Å, respectively.

An examination of these data indicates that both of the ester groups are planar within experimental error and that the bond distances and angles are normal. The similarity of these results with those obtained from electron diffraction studies[5] (vapor phase) and nmr and other spectroscopic investigations[2-4,6] (liquid phase) suggests that the degree of resonance interaction between the alkyl oxygen and carbonyl group is sufficiently

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TABLE I
POSITIONAL PARAMETERS FOR 1,1,2,2-TETRACARBOMETHOXYETHANE

Atom	X	Y	Z
O_1	0.0167 (5[a])	−0.1817 (5)	−0.1617 (3)
O_2	0.1846 (5)	−0.3486 (4)	−0.0139 (3)
O_3	0.3568 (5)	0.1290 (4)	0.0511 (3)
O_4	0.3946 (5)	−0.0936 (4)	0.1729 (3)
C_1	0.0748 (6)	−0.0745 (6)	0.0280 (4)
C_2	0.0865 (5)	−0.2050 (5)	−0.0624 (3)
C_3	0.2102 (9)	−0.4825 (7)	−0.0928 (5)
C_4	0.2926 (6)	0.0015 (5)	0.0843 (4)
C_5	0.6058 (8)	−0.0403 (8)	0.2297 (5)

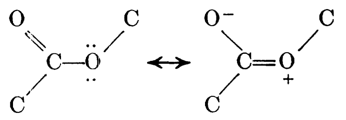
[a] Standard deviations in the least significant figures.

TABLE II
ANISOTROPIC THERMAL FACTORS[a]

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
O_1	5.62	3.45	3.06	0.81	0.04	0.72
O_2	5.58	2.13	3.16	0.85	0.06	0.91
O_3	3.96	3.12	4.45	−0.68	0.93	0.51
O_4	3.52	3.31	3.31	−0.08	0.85	0.23
C_1	3.28	1.88	3.14	−0.22	0.01	0.54
C_2	3.20	2.38	2.85	0.04	0.09	0.31
C_3	4.40	5.14	4.43	−0.08	1.05	−0.13
C_4	6.99	2.83	4.20	1.18	−0.74	1.71
C_5	2.99	2.25	2.38	0.33	−0.01	0.58

[a] These are of the form $\exp[-(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{23}klb^*c^* + 2B_{13}hla^*c^*)]$.

important to constrain the ester group to a planar conformation despite any unfavorable eclipsing interactions that may exist.



Registry No.—1,1,2,2 - Tetracarbomethoxyethane, 5464-22-2.

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The Reaction of Benzyne with Indene

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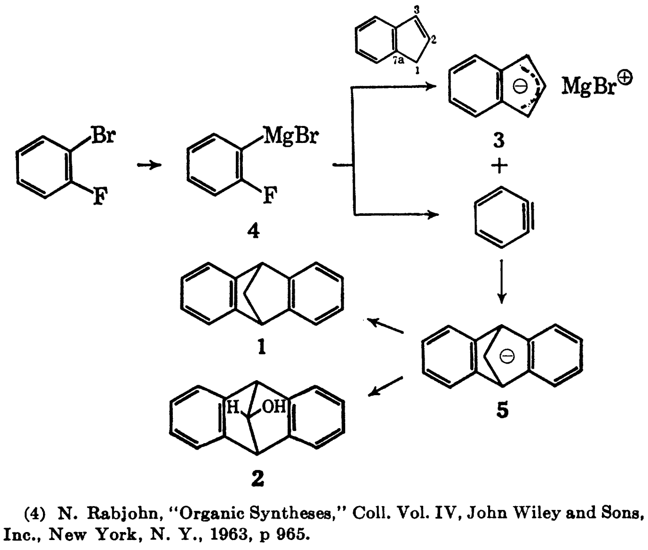
In continuation of a study on the Diels–Alder reaction of indene[1] we now wish to report on its reaction with benzyne. Indene has been shown to give various adducts in which bond formation occurs at the 2,3, at the 1,3, or at the 2,7a positions, depending on the dienophile. Benzyne reacted in the last mentioned fashion with styrene[2] and with α-methylstyrene,[3] which are formally ring-opened indenes.

When benzyne was generated *in situ* in refluxing tetrahydrofuran from *o*-bromofluorobenzene and magnesium[4] in the presence of indene, two products, a $C_{15}H_{12}$ (**1**) and a $C_{15}H_{12}O$ (**2**) species, could be isolated by thin layer chromatography. The nmr spectrum at 60 Mc of **1**, showing an A_2B_2 eight-proton signal in the aromatic region centered at 422.5 cps, a two-proton signal in the benzyl region as a very narrow triplet at 253.4 cps ($W_{1/2}$ = 4.0 cps), and a two-proton signal as a very narrow triplet at 148.7 cps ($W_{1/2}$ = 3.7 cps), indicated a symmetrical molecule. Besides the molecular ion peak of m/e 192, a feature of diagnostic value in the mass spectrum, was a major fragment at m/e 115 indicating indenyl ion (C_9H_7). These data best fit the known 9,10-dihydro-9,10-methanoanthracene (**1**)[5] whose reported melting point and ultraviolet spectrum are identical with ours. The infrared spectrum of **2** revealed the presence of a hydroxyl group at 3568 cm^{-1} and the nmr spectrum (after exchange with deuterium oxide) showed a complex eight-proton signal in the aromatic region centered at about 425, a two-proton triplet at 253, and a one-proton triplet at 262 cps. The melting point and ultraviolet spectrum of **2** are virtually identical with those reported for 9,10-dihydro-9,10-methanoanthracen-11-ol by Meinwald.[6] Identification of our substance as **2** was confirmed by comparison with an authentic sample.

A mechanism for the formation of **1** and **2** accounting for the unexpected presence of **2** could be advanced when it was found that **1** and **2** were not obtained when benzyne was generated from either benzenediazonium-2-carboxylate[7] or diphenyliodonium-*o*-carboxylate.[8] In this view, the carbanionic intermediate **3**, resulting from reaction of the acidic indene with **4**, adds to benzyne. The exact nature of this cycloaddition, whether in one or two steps, is uncertain but a carbanionic species must be involved. This is followed by reaction of the resulting **5** with water leading to **1** and with residual oxygen leading to **2**. It is generally held that organometallic compounds react with oxygen yielding alcohols *via* reduction of the intermediate hydroperoxide anion by carbanion.[9,10]



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