

X-RAY CRYSTAL STRUCTURE OF THE $\text{TiCl}_4 \cdot p\text{-ETHYLANISATE}$ ADDUCT $(\text{TiCl}_4 \cdot \text{O}_3\text{C}_{10}\text{H}_{12})_2$

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(Received July 26th, 1976)

Summary

The molecular and crystal structure of the title compound has been determined by X-ray diffraction. The structure was solved by Patterson and Fourier methods and refined by least-squares techniques to R 0.074 for 2021 independent reflections. Crystals are monoclinic, space group $C2/c$, with 8 $\text{TiCl}_4 \cdot \text{O}_3\text{C}_{10}\text{H}_{12}$ formula units in a unit cell of dimensions $a = 20.464(18)$, $b = 11.331(11)$, $c = 13.430(12)$ Å, $\beta = 104.35(11)^\circ$. The structure is built up from dimeric molecules $(\text{TiCl}_4 \cdot \text{O}_3\text{C}_{10}\text{H}_{12})_2$ which have double chlorine bridges between the two titanium atoms of the dimer. The titanium(IV) atom is octahedrally coordinated by five chlorine atoms and the carbonyl oxygen atom of the *para*-ethylanisate. Changes in the configurations and dimensions from that of the free acceptor and donor molecules are discussed.

Introduction

In the course of the study of $\text{TiCl}_4 \cdot \text{R}_1\text{—COO—R}_2$ adducts, where R_1 and R_2 are alkyl or aryl radicals, a series of products was synthesized in our laboratories [1]. The X-ray crystal structure of the 1 : 1 adduct between TiCl_4 and $\text{C}_2\text{H}_5\text{OCOC}_6\text{H}_4\text{OCH}_3$ (I), is now reported.

Experimental

The crystals of I were firmly mounted in Lindemann glass capillary tubes filled with dry nitrogen and flame sealed. Preliminary space group and unit cell dimensions were obtained from Weissenberg photographs.

A crystal was essentially a parallelepiped, having dimensions ca. $0.40 \times 0.40 \times 0.60$ mm. It was mounted on a Picker FACS 1 four-circle computer controlled diffractometer equipped with a scintillation counter and a pulse-height analyser.

The orientation matrix and cell dimensions were obtained from a least-squares fit of χ , φ , ω , and 2θ values from 12 independent reflections.

Crystal data

TiCl₄O₃C₁₀H₁₂, mol.wt. 329.93, monoclinic $a = 20.464(18)$, $b = 11.331(11)$, $c = 13.430(12)$ Å, $\beta = 104.35(11)^\circ$, $U = 3016.99$ Å³, $D_m = 1.60$, $D_c = 1.628$ g cm⁻³, $Z = 8$. Space group $C2/c$ from systematic absences hkl for $h + k$ odd, $h0l$ for l odd, and from structure determination. Mo- K_α radiation, $\lambda = 0.7107$ Å, $\mu(\text{Mo-}K_\alpha) = 12.80$ cm⁻¹.

Intensity data were collected by use of zirconium-filtered Mo- K_α radiation with $2\theta \leq 50^\circ$. The moving-crystal-moving counter technique was used with a 2θ scan rate of 1° min^{-1} and a scan range of $2.0\text{--}2.50^\circ$, in order to allow for the greater separation of the $K_{\alpha 1}$ and $K_{\alpha 2}$ peaks at increasing 2θ values. Background counts of 10 sec were measured at each end of every 2θ scan.

Three standard reflections, measured after every 50 reflections, showed no fluctuation $> \pm 5\%$ during data collection. 3450 independent reflections were measured of which 2021 were considered observed and had $I \geq 2.5\sigma$ ($\sigma = [N_s + (t_s/t_b)^2 N_b]^{1/2}$; where N_s is the total peak count during the time of scanning t_s , and t_b is the time spent in measuring the N_b background counts. An arbitrary intensity equal to 0.5 the observable limit was assigned to the non significant reflections. All intensities were corrected for Lorentz and polarization effects. No absorption correction was introduced.

Determination and refinement of the structure

The structure of I, was solved by the heavy-atom method. A three-dimensional Patterson map was produced and its interpretation permitted the location of the Ti and Cl atoms. A three-dimensional Fourier map phased on these atoms yielded a clear picture of the whole molecule. It became apparent on the basis of the $C2/c$ space group and of the positional parameters, that the molecule had to be a dimer. The centre of gravity of the dimer was coincident with an inversion centre of the unit cell. The positional and the isotropic thermal parameters of the non-hydrogen atoms were refined by some cycles of block-diagonal least-squares by use of the program of Immerzi [2]. Atomic scattering factors were calculated from the expression in ref. 3, using the values for the parameters given in ref. 4. The weighting scheme of ref. 5 was adopted: $1/w = A + B(F_o) + C(F_o)^2$, where $A = 2 F_o(\text{min})$, $B = 1.0$, and $C = 2/F_o(\text{max})$.

At this point the conventional R was 0.136 for the 2021 nonzero reflections.

Some cycles of block-diagonal refinement were run, assuming anisotropic thermal parameters for all the non-hydrogen atoms of the molecule. The hydrogen atoms were introduced into the calculations but not refined, their coordinates being defined both on stereochemical grounds and on the basis of a three dimensional difference Fourier map. The difference synthesis showed no spurious peaks. The assumed B value for all the hydrogen atoms was 5.0 \AA^2 . The conventional R dropped to 0.074. The final shifts of the atomic parameters were negligible, all being well below the corresponding σ .

Some cycles of block-diagonal refinement were run by assuming the non-centro

TABLE 1

FINAL FRACTIONAL COORDINATES OF THE INDEPENDENT UNIT OF THE TITANIUM(IV) TETRACHLORIDE - *p*-ETHYLANISATE ADDUCT

The estimated standard deviations, in parentheses, in this and in the following tables, refer to the last significant digit

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B</i> (Å ²)
Ti	0.50491(6)	0.66968(12)	0.50801(9)	
Cl(1)	0.51781(9)	0.50369(18)	0.39072(13)	
Cl(2)	0.47982(11)	0.80021(22)	0.61754(17)	
Cl(3)	0.52375(10)	0.79662(20)	0.39099(16)	
Cl(4)	0.61465(9)	0.65207(20)	0.59001(16)	
O(1)	0.4068(2)	0.6600(5)	0.4384(4)	
O(2)	0.3149(2)	0.6385(5)	0.3073(4)	
O(3)	0.1767(3)	0.5526(6)	0.6707(4)	
C(1)	0.3442(3)	0.6365(6)	0.4056(5)	
C(2)	0.3556(4)	0.6715(9)	0.2339(6)	
C(3)	0.3060(5)	0.7163(9)	0.1397(6)	
C(4)	0.2993(3)	0.6109(6)	0.4736(5)	
C(5)	0.3212(4)	0.6350(6)	0.5784(6)	
C(6)	0.2780(4)	0.6151(7)	0.6410(6)	
C(7)	0.2142(4)	0.5674(6)	0.6017(6)	
C(8)	0.1920(4)	0.5399(7)	0.4964(6)	
C(9)	0.2359(4)	0.5623(7)	0.4329(6)	
C(10)	0.1140(4)	0.4847(8)	0.6393(8)	
H(31)	0.255	0.710	0.148	5.0
H(32)	0.310	0.662	0.073	5.0
H(33)	0.317	0.808	0.123	5.0
H(21)	0.384	0.597	0.216	5.0
H(22)	0.391	0.743	0.267	5.0
H(5)	0.372	0.674	0.608	5.0
H(6)	0.293	0.640	0.725	5.0
H(8)	0.141	0.504	0.466	5.0
H(9)	0.219	0.542	0.351	5.0
H(101)	0.089	0.483	0.702	5.0
H(102)	0.122	0.398	0.615	5.0
H(103)	0.080	0.532	0.574	5.0

symmetric *Cc* space group and refining the structure of the dimer (TiCl₄ · C₂H₅COOC₆H₅OCH₃)₂ obtained adding to the atomic coordinates of the monomer the centrosymmetric ones. The refinement did not show any improvement in respect of the refinement performed on the basis of the *C2/c* space group.

Table 1 reports the final fractional coordinates and the corresponding standard deviations of the atoms of the independent unit. Table 2 lists the anisotropic thermal parameters of the non-hydrogen atoms.

Calculated and observed structure amplitudes can be obtained by application to the authors.

Results and discussion

The view of the structure of I adduct molecule is shown in Fig. 1 together with the thermal vibrations ellipsoids. The packing of the molecules is shown in Fig. 2. Both figures have been obtained by means of the ORTEP computing and drawing program [6]. The geometric parameters of the molecule with their esti-

(continued on p. 311)

TABLE 2

ANISOTROPIC THERMAL PARAMETERS (\AA^2), FOR THE NON-HYDROGEN ATOMS OF THE INDEPENDENT UNIT OF IThe temperature factor is in the form: $T_j = \exp -1/4 (B_{11}a^*2j^2 + B_{22}b^*2j^2 + B_{33}c^*2j^2 + 2 B_{12}a^*b^*jk + 2 B_{13}a^*c^*kl + 2 B_{23}b^*c^*kl)$

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
TH						
Cl(1)	2.26(4)	3.95(6)	2.96(5)	-0.48(4)	0.28(4)	0.09(4)
Cl(2)	3.53(7)	4.51(8)	3.01(6)	-0.17(6)	1.11(6)	0.24(6)
Cl(3)	4.12(9)	5.92(11)	4.73(9)	-1.00(8)	1.33(7)	-1.37(8)
Cl(4)	3.95(8)	4.85(9)	4.49(8)	0.01(7)	1.50(7)	1.00(8)
O(1)	2.95(7)	4.07(10)	4.97(9)	-0.18(7)	-0.15(6)	0.21(8)
O(2)	2.96(20)	5.43(28)	3.33(20)	-0.12(19)	0.80(16)	-0.29(19)
O(3)	2.44(18)	6.16(30)	2.89(19)	-0.21(18)	0.38(15)	0.11(19)
C(1)	4.06(24)	5.89(31)	4.95(27)	-0.68(23)	2.04(21)	-0.63(24)
C(2)	2.47(23)	2.53(24)	3.84(28)	-0.12(19)	1.07(21)	-0.05(21)
C(3)	3.16(30)	7.30(53)	3.63(31)	0.33(31)	1.17(25)	0.14(32)
C(4)	4.90(40)	6.08(47)	3.71(32)	0.37(35)	1.38(29)	0.86(32)
C(5)	2.10(22)	3.94(30)	2.97(26)	-0.41(21)	0.50(19)	-0.10(22)
C(6)	3.43(29)	2.93(29)	4.90(36)	-0.78(24)	0.46(26)	-0.21(26)
C(7)	3.25(29)	3.85(32)	4.24(32)	-0.34(24)	1.24(25)	-0.37(26)
C(8)	2.74(27)	2.86(28)	4.61(32)	0.13(22)	1.48(25)	-0.58(24)
C(9)	2.97(27)	4.32(34)	4.73(35)	-0.28(25)	0.50(25)	-0.26(29)
C(10)	4.12(36)	4.36(35)	3.94(30)	0.07(25)	0.94(23)	-0.06(28)
		4.27(40)	7.68(54)	-1.24(29)	3.16(37)	0.11(35)

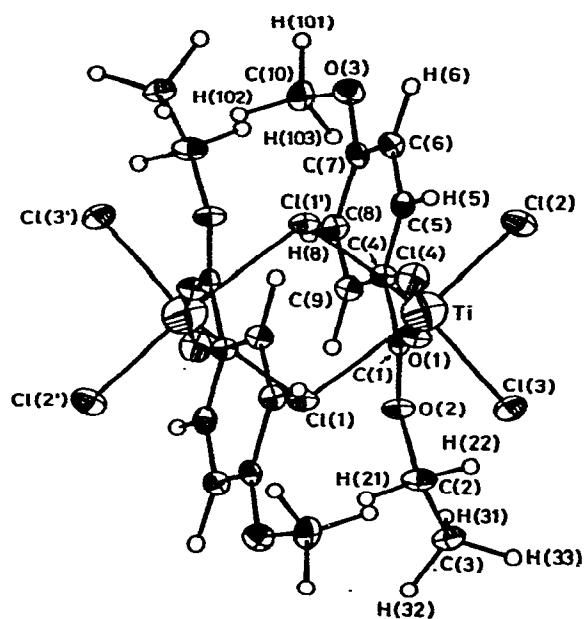


Fig. 1. View of the titanium(IV) tetrachloride - *p*-ethylanisate adduct indicating the atom labelling scheme, and 30% probability thermal vibrations ellipsoids. (' behind atom notations, indicates the atoms related to those of the independent unit by the inversion centre.)

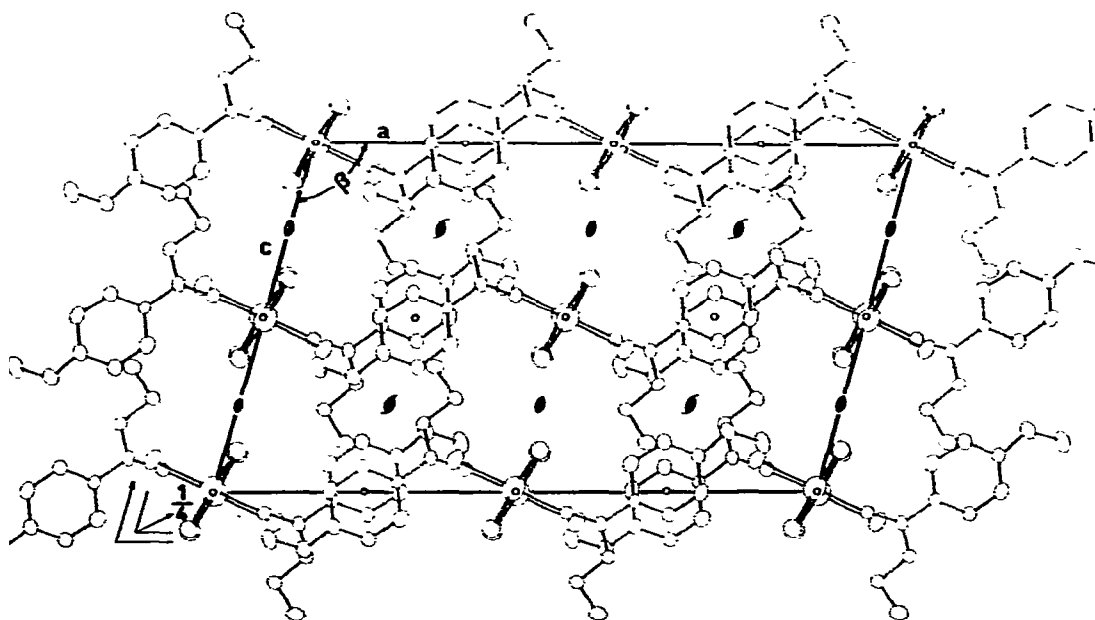


Fig. 2. Packing arrangement of the titanium(IV) tetrachloride - *p*-ethylanisate molecules as viewed down the *b* axis.

TABLE 3

MOST SIGNIFICANT INTRAMOLECULAR BOND LENGTHS AND ANGLES IN THE TITANIUM TETRACHLORIDE - *p*-ETHYLANISATE ADDUCT

(' after atom notations, indicates the atoms related to those of the independent unit by the inversion centre.)

(a) Bond lengths (Å)

Ti-Cl(1)	2.509(2)	C(1)-C(4)	1.48(1)
Ti-Cl(2)	2.234(2)	C(4)-C(5)	1.40(1)
Ti-Cl(3)	2.233(3)	C(5)-C(6)	1.38(1)
Ti-Cl(4)	2.252(3)	C(6)-C(7)	1.39(1)
Ti-Cl(1')	2.498(2)	C(7)-C(8)	1.41(1)
Ti-O(1)	1.997(6)	C(8)-C(9)	1.41(1)
O(1)-C(1)	1.275(9)	C(9)-C(4)	1.39(1)
C(1)-O(2)	1.308(10)	C(7)-O(3)	1.35(1)
O(2)-C(2)	1.488(10)	C(10)-O(3)	1.47(1)
C(2)-C(3)	1.50(2)		

(b) Bond angles (deg.)

Ti-Cl(1)-Ti(1')	100.67(5)	Cl(4)-Ti-O(1)	172.0(1)
Cl(1)-Ti-Cl(3)	88.72(4)	Ti-O(1)-C(1)	169.0(2)
Cl(1)-Ti-Cl(2)	170.7(3)	O(1)-C(1)-O(2)	121.0(3)
Cl(1)-Ti-Cl(1')	79.33(4)	C(1)-O(2)-C(2)	118.8(3)
Cl(1)-Ti-Cl(4)	89.61(4)	O(2)-C(2)-C(3)	105.6(4)
Cl(1)-Ti-O(1)	85.11(9)	O(1)-C(1)-C(4)	123.6(3)
Cl(1')-Ti-Cl(2)	93.34(3)	O(2)-C(1)-C(5)	115.3(3)
Cl(1')-Ti-Cl(3)	167.8(4)	C(1)-C(4)-C(5)	119.5(4)
Cl(1')-Ti-Cl(4)	87.79(4)	C(4)-C(5)-C(6)	119.3(4)
Cl(1')-Ti-O(1)	84.85(9)	C(5)-C(6)-C(7)	120.9(4)
Cl(2)-Ti-Cl(3)	98.34(5)	C(6)-C(7)-C(8)	120.4(4)
Cl(2)-Ti-Cl(4)	95.78(4)	C(7)-C(8)-C(9)	118.3(4)
Cl(2)-Ti-O(1)	88.65(8)	C(8)-C(9)-C(4)	120.4(3)
Cl(3)-Ti-Cl(4)	94.36(5)	C(9)-C(4)-C(1)	119.9(3)
Cl(3)-Ti-O(1)	92.00(10)		

(b) Bond angles (deg.)

C(6)-C(7)-O(3)	115.3(3)	C(7)-O(3)-C(10)	118.2(3)
O(3)-C(7)-C(8)	124.3(4)		

(c) Torsion angles (deg.)

Cl(4)-Ti-O(1)-C(1)	29	C(1)-O(2)-C(2)-C(3)	204
Ti-O(1)-C(1)-C(4)	45	C(6)-C(7)-O(3)-C(10)	190
Ti-O(1)-C(1)-O(2)	-42	C(8)-C(7)-O(3)-C(10)	12
O(1)-C(1)-C(4)-C(5)	13	Cl(2)-Ti-O(1)-C(1)	266
O(1)-C(1)-C(4)-C(9)	194	Cl(3)-Ti-O(1)-C(1)	166
O(1)-C(1)-O(2)-C(2)	-1	Cl(1)-Ti-O(1)-C(1)	80
O(2)-C(1)-C(4)-C(9)	16	Cl(1')-Ti-O(1)-C(1)	0

(d) Most significant intra-molecular distances between non bonded atoms (Å)

Ti...Ti'	3.854(3)	Cl(3)...Cl(4)	3.290(4)
Cl(1)...Cl(1')	3.196(4)	Cl(3)...O(1)	3.047(6)
Cl(1)...Cl(3)	3.322(3)	Cl(1)...O(1')	3.054(5)
Cl(1)...Cl(4)	3.360(3)	Cl(1')...Cl(2)	3.446(4)
Cl(1)...O(1)	3.071(5)	Cl(4)...O(1')	3.57
Cl(2)...Cl(3)	3.380(3)	Cl(4)...O(2')	3.72
Cl(2)...Cl(4)	3.328(3)	Cl(4)...C(1')	3.37
Cl(2)...O(1)	2.961(5)	Cl(4)...C(4')	3.67

(continued)

TABLE 3 (continued)

Cl(4) --- C(9')	3.98	Cl(2) --- C(5)	3.67
Cl(1) --- C(1')	3.76	Cl(3) --- C(2)	3.83
Cl(1) --- C(2)	3.95	O(2) --- C(9)	2.75(1)
Cl(1) --- C(4')	3.95	C(8) --- C(10)	2.85(1)
Cl(1) --- C(5')	3.58	O(1) --- C(2)	2.69(1)
Cl(2) --- C(1)	3.92	O(1) --- C(5)	2.89(1)

mated standard deviations are reported in Table 3.

The carbonyl oxygen of the *p*-ethylanisate acts as the donor atom. The adduct of titanium(IV) tetrachloride with *p*-ethylanisate is a dimer ($\text{TiCl}_4 \cdot \text{C}_2\text{H}_5\text{COOC}_6\text{H}_4\text{OCH}_3$)₂ containing two Ti—Cl—Ti bridges. Such double chlorine bridges have previously been found in several adduct molecules: ($\text{TiCl}_4 \cdot \text{POCl}_3$)₂ [7], ($\text{TiCl}_4 \cdot \text{CH}_3\text{COOC}_2\text{H}_5$)₂ [8].

In I and in the reported adducts the acceptor molecule (TiCl_4) has changed its coordination from tetrahedral to octahedral.

In I the Ti—Cl and Ti—O bond lengths and the Cl—Ti—Cl and Cl—Ti—O bond angles correspond to a slightly distorted octahedron and are essentially similar to those reported for ($\text{TiCl}_4 \cdot \text{CH}_3\text{COOC}_2\text{H}_5$) and ($\text{TiCl}_4 \cdot \text{POCl}_3$)₂.

The average value of the Ti—Cl bridge distances found in I is 2.50 Å, and this value is in fairly good agreement with the Ti—Cl separations found in the α and γ crystalline modifications of TiCl_3 and for crystalline TiCl_2 that are 2.51 Å [9–12]. For the latter compounds all the chlorine atoms act as bridges between titanium atoms.

For I and the reported adducts the lengths of the octahedral non-bridging Ti—Cl bonds appear to be slightly longer than the tetrahedral Ti—Cl bond lengths of 2.18 ± 0.04 Å found in free TiCl_4 [13]. The Ti—O distance in I of 1.997(6) Å is a little shorter than the corresponding distances of 2.029(3) and 2.10(2) Å reported in ref. 8 and ref. 7, respectively. Discussion of the effects of adduct formation on the donor molecule would be assisted by informations on the dimensions and configuration of free *p*-ethylanisate.

No direct experimental data are available, but we have derived the most probable values of the oxygen—carbon distances of the O=C carbonyl group, and of the C—O and O-ethyl groups of free *p*-ethylanisate from values found for similar compounds. The comparison between the literature values and the values found

TABLE 4
COMPARISON BETWEEN THE OXYGEN—CARBON DISTANCES IN ESTERS AND IN ADDUCTS (Å)

	a	b	c	d
—C=O carbonyl	1.23(1)	1.21(1)	1.234(5)	1.275(9) O(1)—C(1)
=C—O—	1.36(1)	1.34(1)	1.295(5)	1.308(10) C(1)—O(2)
—O—CH ₂ —CH ₃	1.43(1)	1.45(1)	1.495(5)	1.488(10) O(2)—C(2)

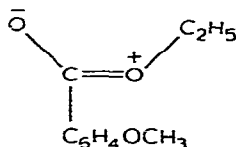
^a Average values found in free esters ref. 14. ^b Average values found in racemic bis(ethylfumarate)(acetonitrile)nickel(0) [15], and in racemic bis(ethylfumarate)bis(acetonitrile)cobalt(0) [16]. ^c Values found in the $\text{TiCl}_4 \cdot \text{CH}_3\text{COOC}_2\text{H}_5$ adduct, ref. 8. ^d Values found in the $\text{TiCl}_4 \cdot \text{C}_2\text{H}_5\text{OCOC}_6\text{H}_4\text{OCH}_3$ adduct, the present work.

in this work are reported in Table 4. The coordination of the carbonyl carbon in I is nearly planar. The least-squares plane defined by C(1), O(1), O(2) and C(4) and the distances of the atoms from the plane are reported in Table 5.

The O(1)—C(1) and O(2)—C(2) bonds are nearly eclipsed, while the C(2)—C(3) bond is nearly *trans* in respect to the C(1)—O(2) bond. The least-squares plane defined by the atoms of the benzene ring of *p*-ethylanisate residue (C(4), C(5), C(6), C(7), C(8) and C(9)) and the distances of the atoms from the plane are reported in Table 5. A dihedral angle of $15^{\circ}12'$ was found between this plane and that defined by O(1), C(1), O(2) and C(2). The relatively high value of the dihedral angle between these two planes seems to be due to steric hindrance between the H(5) hydrogen atom, and Cl(2) and Cl(1') atoms. The Cl(2) ... H(5) and Cl(1') ... H(5) separations are 2.60 and 3.05 Å and would be 2.78 and 2.53 Å, respectively, if the dihedral angle were 0° . The high value of this dihedral angle may arise from packing requirements. The changes in *p*-ethylanisate residue on adduct formation in I are an increase of the carbonyl C=O bond length to 1.275(9) Å, a shortening of the C(1)—O(2) bond to 1.31(1) Å, and a lengthening of the ethyl-oxygen bond to 1.49(1) Å.

The carbon-carbon bonds C(1)—C(4) and C(2)—C(3) are 1.48(1) and 1.50(2) Å, respectively (see Table 4). These changes in the free *p*-ethylanisate molecule may be explained as a result of the electron density withdrawal from the donor molecule to the acceptor titanium atom.

The carbonyl C=O bond will thus be more polar, and the adjacent C(1)—O(2) bond less polar owing to the electron density drift. In the same time the ethyl-oxygen bond will become more polar and thus weaker. Delocalization will be favoured according to the scheme:



It follows that the major contributor to the resonance hybrid may be the structure shown in Fig. 3. All intramolecular distances are satisfactory (see Table 3). The packing consists in the arrangement of up and down molecules about the intermolecular inversion centres of the unit cell. The intermolecular distances

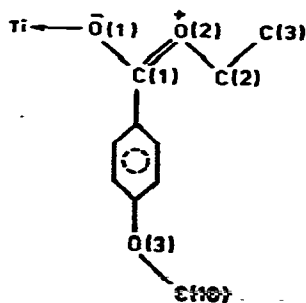


Fig. 3. A schematic drawing of the structure of the major resonance contributor of I.

TABLE 5

EQUATIONS OF THE LEAST-SQUARES PLANES AND DISPLACEMENTS OF ATOMS FROM THESE PLANES FOR THE *p*-ETHYLANISATE RESIDUE OF I

Each plane is represented by an equation of the type $lx + my + nz - P = 0$, referred to an orthogonal system of axes which has x along the a^* axis, y in the $(b - c)$ plane and z along the c axis.

(a) O(1), C(1), O(2) and C(4)

$$-0.2030x + 0.9735y + 0.1050z - 6.0383 = 0$$

Atomic displacements (Å)

O(1)	0.0052	} root mean square distance 0.016
C(1)	-0.0141	
O(2)	0.0047	
C(4)	0.0043	

(b) Phenyl ring (C(4) ... C(9))

$$0.3764x - 0.9223y + 0.0882z + 3.7112 = 0$$

Atomic displacements (Å)

C(4)	-0.0126	} root mean square distance 0.012
C(5)	0.0143	
C(6)	-0.0074	
C(7)	-0.0011	
C(8)	0.0028	
C(9)	0.0041	

are satisfactory, no Cl ... Cl, Cl ... C, O ... O, O ... C, and C ... C distance being lower than 3.45, 3.60, 3.51, 3.50, and 3.55 Å, respectively.

Acknowledgements

We thank prof. U. Giannini and R. Mazzocchi for providing the crystals and Prof. P. Corradini for his interest, advice, and useful suggestions.

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