Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

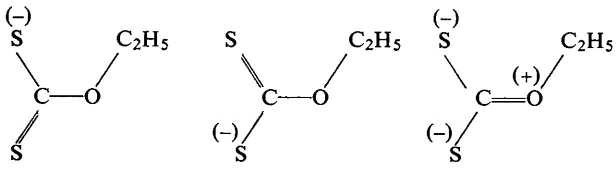
Acta Cryst. (1971). B**27**, 2491

The O–C (sp^3) single-bond distance. By S. Merlino, *Istituto di Mineralogia dell'Università di Pisa, Italy*

(*Received* 13 *July* 1971)

Recent structural data show that the lengthening of the O–C bond in the group $\mathrm{C{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}C}$ (in esters and lactones) is related to the contribution of the resonance form $\mathrm{C{-}\underset{\underset{\displaystyle O^{(-)}}{|}}{C}{=}O^{(+)}{-}C}$. This structural feature can be explained in terms of a smaller ionic contribution to the bond in question.

The structure of the ethylxanthate group, as found by the X-ray crystal structure determination of several metal xanthates, can be described as resonating among the following canonical forms:



(I) (II) (III)

From the lengths of the sulphur-to-carbon and carbon-to-oxygen bonds, the relative weights of the three resonance forms can be calculated. In Table 1 some structural features, obtained from recent determinations of good accuracy of the crystal structures of metal ethylxanthates, are reported. This Table shows in the first two columns the central C–O bond distance and the oxygen to ethyl carbon distance, and in the third column the contribution of the resonance structure (III) as determined from the S–C and C–O bond lengths (Merlino, 1969; Merlino & Sartori, 1971).

The value given for carbon-to-oxygen bond distances found in paraffinic alcohols is 1·426 Å (*Chemical Society Special Publication*, 1958, 1965). It appears from Table 1 that whenever in the ethylxanthate group the resonance form $S_2^{(-)}C{=}O^{(+)}R$ gives a substantial contribution, there is a highly significant lengthening of the bond distance between the oxygen atom and the carbon atom of the ethyl group.

A similar lengthening was also noted in the lactone group $\mathrm{{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}C{-}O{-}C}$ for the oxygen-to-carbon bond in the β position relative to the C=O group, by Kalyani & Vijayan (1969). They explained it as 'probably due to the strain introduced as a result of the group being part of a ring system'. However the explanation is untenable in the case of the similar lengthening observed in esters (Bracher & Small, 1967). It should be noted that also in the $\mathrm{C{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}C}$ group there is a contribution by the resonance structure $\mathrm{C{-}\underset{\underset{\displaystyle O^{(-)}}{|}}{C}{=}O^{(+)}{-}C}$, which results in a shortening of the carbon-to-oxygen bond adjacent to the carbonyl group. Then it can be argued that, as in the ethylxanthate group, also in the $\mathrm{C{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}C}$ group the noteworthy lengthening of the oxygen-to-alkyl-carbon bond is in dependence on a substantial contribution of the resonance form $\mathrm{C{-}\underset{\underset{\displaystyle O^{(-)}}{|}}{C}{=}O^{(+)}{-}C}$. This was confirmed by a thorough search of the crystal structures of compounds containing the group $\mathrm{C{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}C}$, published in *Acta Crystallographica* in the last four years (1967–1970). The data from crystal structure determinations of high accuracy (e.s.d. for C–O bonds

Table 1. *Structural features of metal ethylxanthates*

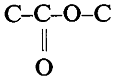
E.s.d.'s are given in parentheses.

C–O	O–C	% (III)	
1·359 (17) Å	1·431 (17) Å	13	Cobalt(III) tris(*O*-ethylxanthate) (*1*)
1·328 (10)	1·476 (10)	22	Iron(III) tris(*O*-ethylxanthate) (*2*)
1·297 (11)	1·471 (11)	30	Chromium(III) tris(*O*-ethylxanthate) (*3*)
1·331 (6)*	1·477 (8)*	22	Sodium ethylxanthate dihydrate (*4*)

* weighted mean value

(*1*) Merlino (1969), (*2*) Hoskins & Kelly (1970), (*3*) Merlino & Sartori (1972), (*4*) Mazzi, Tazzoli & Ungaretti (1969).

Table 2. *Structural features in the group*



$$\mathrm{C{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}O{-}C}$$

E.s.d.'s are given in parentheses.

C–O	O–C	
1·365 (6) Å	1·438 (6) Å	Δ-8,14-Anhydrodigitoxigenin (*1*)
1·364 (4)	1·447 (5)	1:1 Procaine–bis-*p*-nitrophenyl phosphate complex (*2*)
1·358 (6)	1·448 (4)	Sodium ascorbate (*3*)
1·358 (5)	1·464 (5)	D-Galactono-γ-lactone (*4*)
1·355 (2)*	1·444 (2)*	L-Ascorbic acid (*5*)
1·342 (4)	1·472 (4)	Ethyl carbamate (−105 °C) (*8*)
1·340 (5)	1·475 (5)	β-D-Glucurono-γ-lactone (*6*)
1·337 (3)	1·462 (2)	*N*-Methyl-5,5-dimethyloxazolidine-2,4-dione (*7*)
1·333 (4)	1·473 (4)	Ethyl carbamate (25 °C) (*8*)
1·331 (7)	1·478 (7)	6β-7β-Methylene-17β-hydroxyandrost-4-en-3-one 17-acetate (*9*)
1·330 (3)	1·482 (3)	Solstitialin (*10*)
1·329 (5)	1·360 (5)	Quinuclidinyl di-α,α′-thienylglycollate (*11*)
1·323 (4)	1·486 (4)	*trans*-Bicyclo[4·2·0]octyl 1-3,5-dinitrobenzoate (*12*)

* weighted mean value

(*1*) Gilardi & Karle (1970), (*2*) Sax, Pletcher & Gustaffson (1970), (*3*) Hvoslef (1969), (*4*) Jeffrey, Rosenstein & Vlasse (1967), (*5*) Hvoslef (1968), (*6*)Kim, Jeffrey, Rosenstein & Corfield (1967), (*7*) Kistenmacher & Stucky (1970), (*8*) Bracher & Small (1967), (*9*) Braun, Hornstra & Leenhouts (1970), (*10*) Thiessen & Hope (1970), (*11*)Meyerhöffer (1970), (*12*) Barnett & Davis (1970).

≤0·007 Å) are reported in Table 2. This Table shows in the first column the distances of the C–O bond adjacent to the carbonyl group and in the second column the distances of the O–C bond in the β position relative to the carbonyl group. The data are arranged in order of increasing contribution by the resonance form $\mathrm{C{-}\underset{\underset{\displaystyle O^{(-)}}{|}}{C}{=}O^{(+)}{-}C}$, as measured by the decrease in the C–O bond distances. It appears from the data that there is a progressive lengthening of the O–C bond distances.

This structural feature can be explained in terms of a smaller ionic contribution to the bond in question. It is well known that bonds between atoms of different electronegativities present an extra ionic resonance energy (Pauling, 1960): for the O–C bond the contributing ionic form is O^-C^+. From the Schomaker & Stevenson (1941) formula for the O–C bond length:

$$d_{OC}=r_O+r_C-0{\cdot}09\ |x_O-x_C|$$

(where r_O, x_O and r_C, x_C are the covalent radii and electronegativities of oxygen and carbon atoms) we can calculate a contraction of O–C distance from 1·51 to 1·42 Å due to the ionic contribution.

When there is a relevant contribution of resonance forms of the type $\mathrm{S_2^{(-)}C{=}O^{(+)}R}$ or $\mathrm{C{-}\underset{\underset{\displaystyle O^{(-)}}{|}}{C}{=}O^{(+)}{-}R}$, there is also the displacement of a partial positive charge on the oxygen atom. This displacement diminishes the strength of the ionic structure O^-C^+ (with the displacement of a unit positive charge on the oxygen atom the ionic bond would become a non-bonded contact OC^+), with a consequent lengthening of the bond over the value of 1·42 Å.

References

Barnett, B. L. & Davis, R. E. (1970). *Acta Cryst.* B**26**, 326.

Bracher, B. H. & Small, R. W. H. (1967). *Acta Cryst.* **23**, 410.

Braun, B. P., Hornstra, J. & Leenhouts, J. L. (1970). *Acta Cryst.* B**26**, 352.

Chemical Society Special Publication (1958). No. 11.

Chemical Society Special Publication (1965). No. 14.

Gilardi, R. D. & Karle, I. L. (1970). *Acta Cryst.* B**26**, 207.

Hoskins, B. F. & Kelly, B. P. (1970). *Chem. Commun.* p. 45.

Hvoslef, J. (1968). *Acta Cryst.* B**24**, 23.

Hvoslef, J. (1969). *Acta Cryst.* B**25**, 2214.

Jeffrey, G. A., Rosenstein, R. D. & Vlasse, M. (1967). *Acta Cryst.* **22**, 725.

Kalyani, V. & Vijayan, M. (1969). *Acta Cryst.* B**25**, 253.

Kim, S. H., Jeffrey, G. A., Rosenstein, R. D. & Corfield, P. W. R. (1967). *Acta Cryst.* **22**, 733.

Kistenmacher, T. J. & Stucky, G. D. (1970). *Acta Cryst.* B**26**, 1445.

Mazzi, F., Tazzoli, V. & Ungaretti, L. (1969). *Atti Accad. Naz. Lincei, Cl. Sc. fis. mat. e nat.* **47**, 69.

Merlino, S. (1969). *Acta Cryst.* B**25**, 2270.

Merlino, S. & Sartori, F. (1971). *Acta Cryst.* In the press.

Meyerhöffer, A. (1970). *Acta Cryst.* B**26**, 341.

Pauling, L. (1960). *The Nature of the Chemical Bond,* 3rd ed. Ithaca: Cornell Univ. Press.

Sax, M., Pletcher, J. & Gustaffson, B. (1970). *Acta Cryst.* B**26**, 114.

Schomaker, V. & Stevenson, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37.

Thiessen, W. E. & Hope, H. (1970). *Acta Cryst.* B**26**, 554.