152. Structural Characteristics of the Carboxylic Ester Group

by **W. Bernd Schweizer** and **Jack D. Dunitz**

Laboratorium für Organische Chemie, ETH-Zentrum, CH-8092 Zürich

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Summary

Average bond distances and bond angles in carboxylic esters with different substitution patterns have been derived by analyzing data from many crystal structures retrieved from the *Cambridge Structural Database* (CSD). Conformational preferences in the attachment of substituents are found.

In constructing molecular models it is frequently assumed that a given chemical grouping is adequately described by a standard set of bond distances and angles, together with certain conformational regularities. It is of interest to enquire how well this assumption actually holds for common chemical groupings. In the present study we take up the question for the ester group. A parallel study of the amide group has also been done [1].

Selection of data. – The experimental information for our study was taken from the *Cambridge Structural Database* ((CSD), version of May 1980 with 26978 entries in the bibliographic file [2][1]). A search of the connectivity file for the C–CO–O–C fragment yielded a subfile containing 1750 entries. For *Table 1A*

Table 1. *Standard dimensions* (distances in Å, angles in degrees) *of various types of carboxylic esters, R′. COOR based on structures with σ(C–C) ≤ 0.005 Å* (see *Fig. 1* for explanation of symbols)

A

	N	*a*	*b*	*c*	*d*	*ab*	*bd*	*bc*	*cd*
R'COOR	118	1.447(13)	1.340(14)	1.495(19)	1.195(7)	117.4(1.6)	123.4(9)	111.2(1.0)	125.4(1.2)
ArCOOR	27	1.445(12)	1.343(14)	1.484(12)	1.199(6)	117.2(1.6)	123.4(9)	111.6(8)	125.0(1.2)
R'COOAr	11	1.402(13)	1.352(20)	1.497(16)	1.191(5)	118.9(1.7)	122.7(1.1)	110.6(8)	126.7(1.6)
γ-Lactones	10	1.462(8)	1.350(9)	1.515(13)	1.198(7)	110.2(1.4)	121.7(9)	109.7(1.2)	128.6(8)
δ-Lactones	6	1.462(13)	1.337(8)	1.514(15)	1.204(7)	122.9(2.9)	118.5(1.0)	118.4(1.7)	123.0(1.2)

B

R	N	*a*	*b*	*ab*	*bd*
$C(H_3)$	103	1.448(8)	1.329(9)	116.3(8)	123.6(14)
$C(C,H_2)$	37	1.4542(8)	1.336(12)	116.5(11)	123.1(14)
$C(C_2,H)$	77	1.449(11)	1.344(13)	117.5(13)	123.2(11)
$C(C_3)$	9	1.473(7)	1.344(11)	120.8(18)	123.8(16)
C(AROM.)	10	1.402(12)	1.355(10)	118.5(19)	122.6(13)

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[1]) On file locally through the Affiliated Data Centre for Switzerland, Organic Chemistry Laboratory, ETHZ (details available from *W.B.S.*)

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we made four searches of this subfile for the fragments: $C(sp^3){-}CO{-}O{-}C(sp^3)$, cyclic and acyclic separately; $C(sp^3){-}CO{-}O{-}C_{ar}$ and $C_{ar}{-}CO{-}O{-}C(sp^3)$. Structural parameters were calculated with the programm *GEOM 78* [2] for fragments in each class selected according to the following criteria: diffractometer data, entry must contain atomic coordinates for H-atoms, mean $\sigma(C{-}C)$ must be ≤ 0.005 Å, R must be ≤ 0.075, no disorder, no error flag. The resulting lists from *GEOM 78* were then inspected to remove entries for structures containing heavy atoms as well as data from undesired ester groups in entries with multiple ester fragments²).

In addition, for *Table 1B* and for the histograms, *etc.*, we made connectivity searches³) for the fragments:

$$C{-}CO{-}O{-}R \text{ with } R = CH_3, CH_2{-}C, CH{-}(C)_2, C{-}(C)_3, Ph;$$
$$R'{-}CO{-}O{-}C \text{ with } R' = CH_2{-}C, CH{-}(C)_2, C{-}(C)_3, Ph.$$

For *Table 1B*, the same selection criteria were applied as for *Table 1A* except that heavy-atom structures were not removed. Also entries with $\sigma(C{-}C) \leq 0.02$ Å were accepted for the histograms and scatter-plots *(Figs. 2–5)* involving torsion angles.

Dimensions of carboxylic ester groups. – *Table 1* shows that bond distances and angles in the ester group vary detectably, depending on the nature of the substituents (R–COOR', Ar–COOR, R–COOAr) for (*E*)-esters and depending on ring size for (*Z*)-esters (lactones). The variability within each subgroup is larger than the scatter expected from the standard deviations of the individual measurements; it is probably real and due to further differences among the substituents, which are ignored in the present study. A more detailed study of these differences could well be rewarding. Note, however, the remarkable constancy of the C,O-carbonyl bond lengths, both within the subgroups and altogether. The carbonyl bond in an ester seems to be about 0.03 Å shorter than in an amide [1]. Another interesting result is the difference between the O–C=O (*bd*) and C–C=O (*cd*) bond angles; the former is always the smaller, the difference amounting to 7° for the γ-lactones.

The dimensions given in *Table 1* are obtained from mean atomic positions in molecular crystals mainly at room temperature. Interatomic distances from such data tend to be too short (by ~ 0.01–0.02 Å) because of the effects of rigid-body and

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²) One problem with the present version of the CSD is that the programs *CONNSER* (searches for structures containing fragments with a given connectivity) and *GEOM 78* (calculation of specified geometrical parameters for given fragments) utilize different types of information contained in the files. *CONNSER* uses chemical connectivity information stored in the connectivity file, while *GEOM 78* uses a connectivity table based on interatomic distances calculated from atomic coordinates stored in the data file. Thus, for example, with *CONNSER* a data subfile containing all structures with cyclic esters (lactones) can be constructed. The geometric parameters of such esters can then be computed, listed and compared with *GEOM 78*. However, if a structure on the subfile contains more than one ester group, *GEOM 78* cannot distinguish the cyclic from the acylic ones and will hence compute and list parameters for all of them. At present, in such cases, the undesired information has to be recognized by inspection and removed manually, and it is possible that some of it has eluded our scrutiny.

³) But based on the version of September, 1980 with 27988 entries in the bibliographic file (1787 referring to C–CO–O–C fragments).

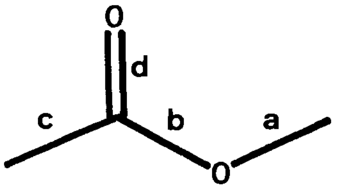

Fig. 1. *Explanation of symbols used in* Table 1

internal molecular vibrations in the crystal [3]. This possible systematic error should affect the various classes of esters about equally but it would have to be taken into account in making comparisons with parameters obtained by other methods, *e.g.* gas-phase electron diffraction or *ab initio* calculations. Bond angles should be much less affected.

There is not a single example of an acyclic (*Z*)-ester, and indeed it is very unusual for the *cba (Fig. 1)* torsion angle in an acyclic ester to deviate by more than about 10° from the antiperiplanar arrangement. It would thus appear that esters only adopt the (*Z*)- or *cis*-configuration when compelled to do so by ring constraints.

Preferred conformations of substituents. – In spite of the enormous heterogeneity in the nature of the substituents certain fairly pronounced conformational regularities are discernable. We have summarized the conformations of alkyl and aryl substituents at the O-atom in the form of histograms shown in *Figure 2.* Esters of primary alcohols usually have the C–O–C–C torsion angle close to 180°, *i.e.* the C,C-bond is antiperiplanar *(app)* to the ester C,O-bond. The exceptions are numerous enough to indicate that the preference for the *app*-orientation can easily be outweighed by other factors. Esters of tertiary alcohols follow the same pattern; one of the three C,C-bonds is *app* to the ester C,O-bond (the histogram shows only the distribution of the *smallest* of the three C–O–C–C torsion angles; approximate values of the other two angles are obtained by adding $\pm 120°$ to the given angle). For esters of secondary alcohols the conformational pattern is different; neither of the C,C-bonds is usually near the *app*-position, but the C–O–C–H torsion angle invariably lies in the range 0-60° and mostly in the range 0-30°, *i.e.* the C,H-bond is usually synperiplanar to the ester C,O-bond, as first noted by *Mathieson* [4].

In aryl esters the plane of the aromatic system does not coincide with the plane of the ester group but tends to be nearly perpendicular to it. As seen in *Table 1,* the O,C-bond *a* in an aryl ester is nearly 0.05 Å shorter than when the C-atom belongs to an alkyl group, indicating that phenol-type conjugation is by no means suppressed in this type of conformation. It seems clear, however, that any such conjugation would have to be with the sp^2 lone pair of the O-atom and not with the *p* lone pair.

Another regularity found in aryl esters is that the substituted C-atom is always slightly displaced from the plane formed by its three bonded atoms. The deviation is small (up to *ca.* 0.05 Å for 11 examples with $\sigma(\mathrm{C{-}C}) \leq 0.005$ Å) but systematic; the displacement of the C-atom from the plane is always towards the carbonyl O-atom, *i.e.* in the opposite direction to the sp^2 lone pair of the ester O-atom. For a phenyl substituent this kind of displacement would correspond to a bending of the

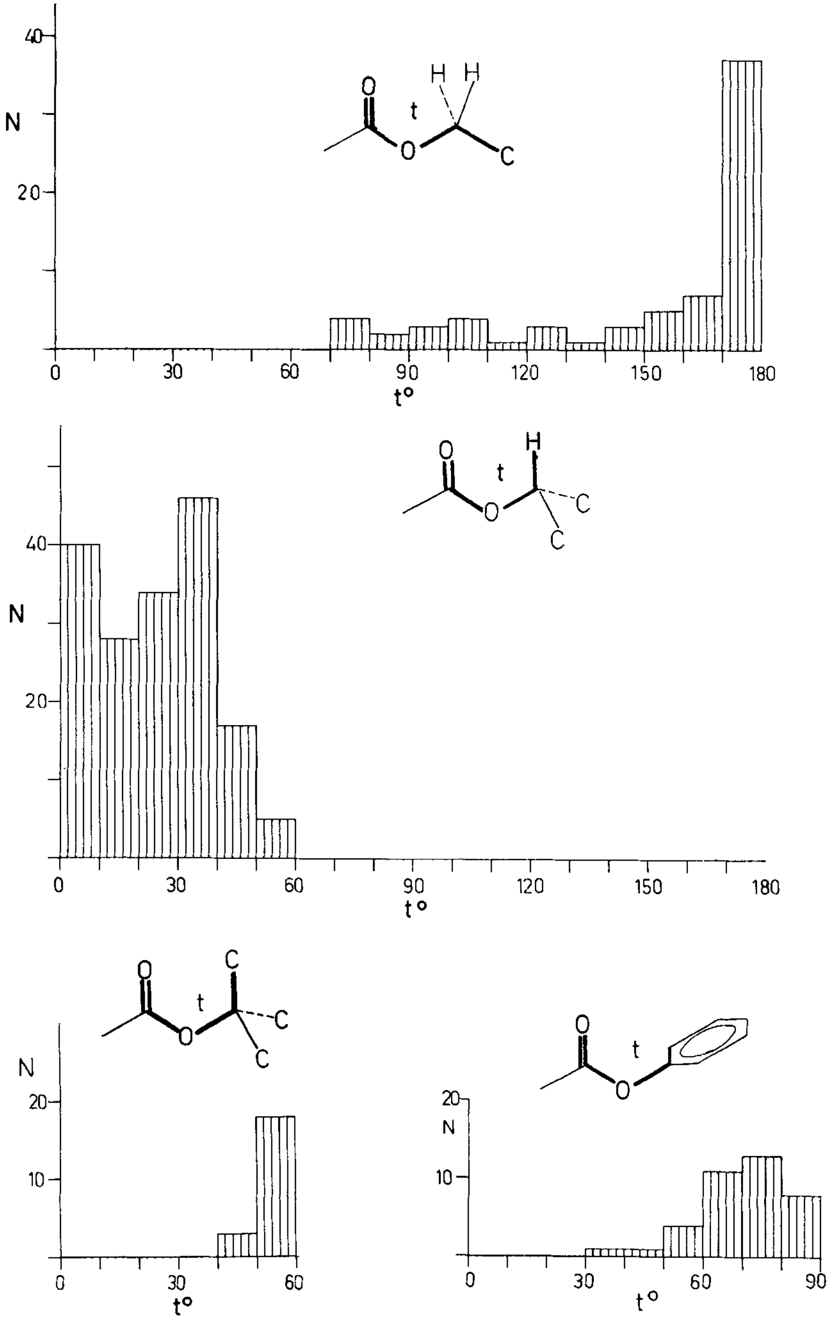

Fig. 2. *Histograms of C–O–C–C (or C–O–C–H) torsion angles* t (absolute values in degrees) *in carboxylic esters derived from primary, secondary, and tertiary alcohols and from phenols* (Of the three possible |*t*| values for the tertiary case, only the one in the range 0–60° is counted; for the phenolate esters only the smaller of the two possible |*t*| values is counted)

C(1), C(4)-axis out of linearity with the O, C(1)-phenolic bond, towards the sp^2 lone pair.

Esters of tertiary alcohols show an analogous but even more pronounced distortion at the substituted C-atom. The bond angle O–C–C (in plane) is consistently about 7° smaller than the tetrahedral angle, and the other two O–C–C angles are about equal to or slightly larger than the tetrahedral angle *(Table 2)*. In other words, the approximate threefold axis of the tertiary substituted C-atom does not point along the C, O-bond direction but deviates in a systematic way from it. Of the three C–C–C bond angles, the one opposite to the in-plane O–C–C angle tends to be the largest. Similar distortions have been reported for tertiary silyl nitronates [5] and for *t*-butoxy and *t*-butylthio groups [6]. There is an obvious similarity to the 'methyl tilt', the deviation of the approximate symmetry axis of the methyl group from the C, X-bond direction in molecules such as methanol[4]).

For esters of primary alcohols the O–C–C bond angle appears to be correlated with the torsion angle about the O, C-bond *(Figure 3a)*. When the C, C-bond lies in the plane of the ester group the O–C–C bond angle tends to be a few degrees smaller than the tetrahedral angle, just like in-plane O–C–C bond angle of a tertiary substituted C-atom; when the C, C-bond makes a steep angle to the plane the O–C–C bond angle tends to be slightly larger than the tetrahedral angle, again similar to the tertiary case.

We were surprised to find just the opposite correlation for esters of secondary alcohols *(Figure 3b)*. Here, the larger of two O–C–C bond angles is for the C-atom

Table 2. *Values of $C–O–C–C_l$ torsion angles* t *and of $O–C–C_i$ and $C_i–C–C_j$ bond angles a_i and β_{ij} in esters derived from tertiary alcohols listed under their CSD-acronyms* (the tilt angle is defined as $(2a_1-a_2-a_3)/3$

	t	a_1	a_2	a_3	β_{12}	β_{13}	β_{23}	Tilt
AOTETC	179.3	101.84	112.75	110.89	107.25	110.25	113.19	-3.33
AXMCHD	173.0	101.10	113.96	109.80	106.79	111.68	112.88	-3.59
AXMCHD	164.2	101.28	110.02	109.00	109.08	113.96	112.87	-2.74
CLIVOR	-165.9	104.73	109.72	109.29	108.43	113.47	111.00	-1.59
CYPROT	178.5	105.30	111.38	109.67	103.16	112.11	114.70	-1.74
DAXDOD	178.4	104.72	113.41	112.17	109.26	108.90	108.24	-2.78
DELPSC	174.4	101.45	109.94	108.03	113.60	108.78	114.17	-2.51
DEXPOX	-176.4	102.86	109.53	109.51	112.75	111.91	110.02	-2.22
DEXPRO	-178.6	102.25	110.23	109.00	111.64	111.26	112.01	-2.45
DHPHYT	-177.2	102.25	109.81	108.36	113.69	109.71	112.44	-2.28
DIFERM	-176.6	101.85	111.09	110.67	108.91	111.67	112.18	-3.01
HIMLBU	177.6	102.51	110.42	109.04	112.39	109.70	112.31	-2.41
MBYXBI	-177.3	104.60	112.12	111.51	110.48	109.39	108.69	-2.40
MXTZOC	-176.5	100.98	109.78	109.48	112.27	111.43	112.30	-2.88
NPRXML	178.9	102.74	109.73	109.33	111.44	110.82	112.35	-2.26
PROCLB	-178.9	101.58	109.64	108.76	109.23	111.69	115.08	-2.54
PRODBR	-179.9	101.66	110.92	109.38	108.89	111.09	114.19	-2.83
PROGDC	175.4	105.86	110.68	109.19	103.14	111.75	115.67	-1.36
PRXPRT	175.8	102.97	106.92	103.12	105.55	111.52	124.65	-0.68
SIRCDA	-165.7	105.87	113.60	111.18	106.04	103.23	115.72	-2.17
TBCMTB	180.0	101.74	109.18	109.10	111.40	111.07	113.66	-2.47

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[4]) From a recent theoretical analysis [7] it is proposed that the methyl tilt is to be ascribed mainly to bond-bond repulsions. Whether this interpretation also holds for the angular deviations observed here is an open question.

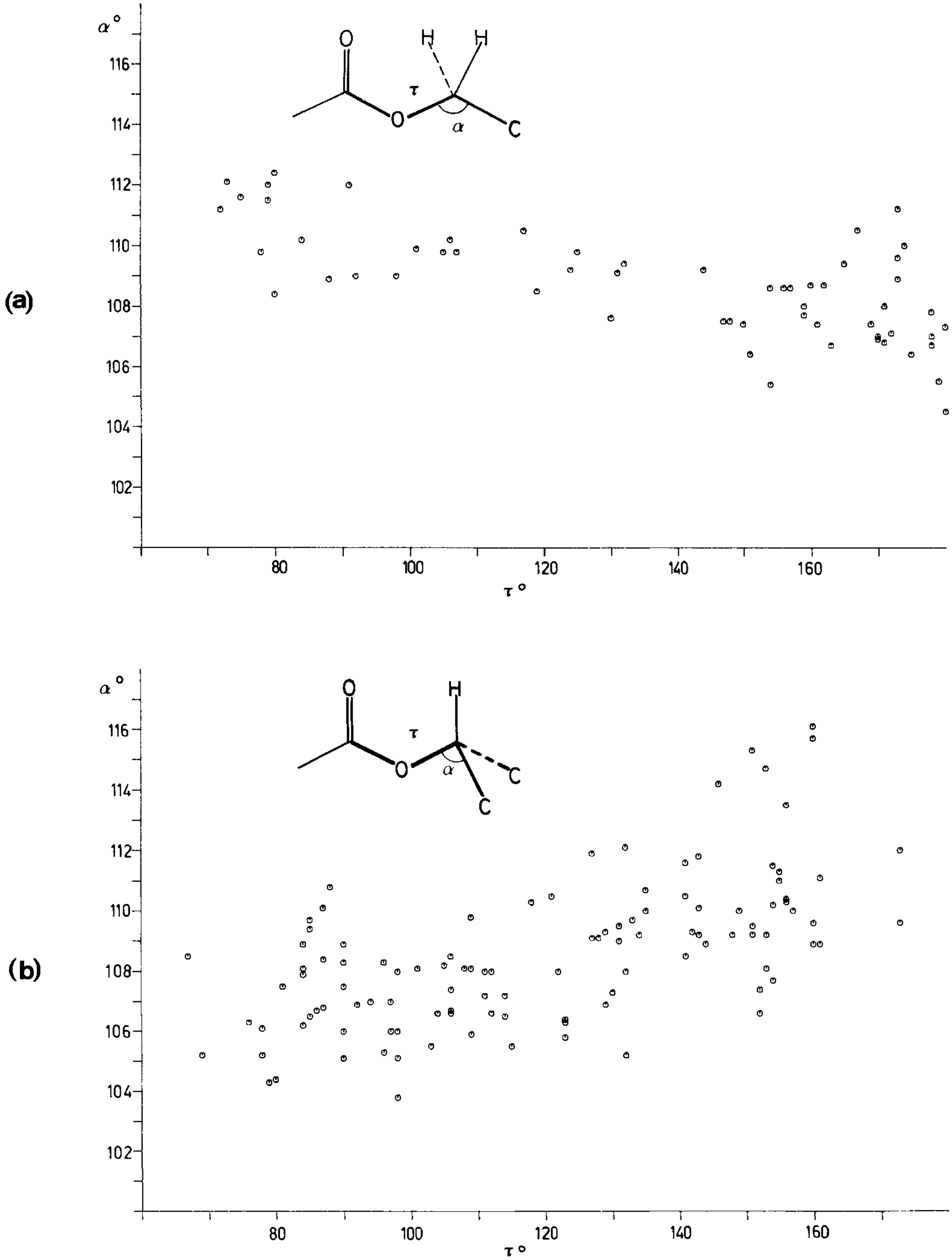

Fig. 3. *Scatter-plots of C–O–C–C torsion angle τ* vs. *O–C–C angle α in esters derived from (a) primary and (b) secondary alcohols*

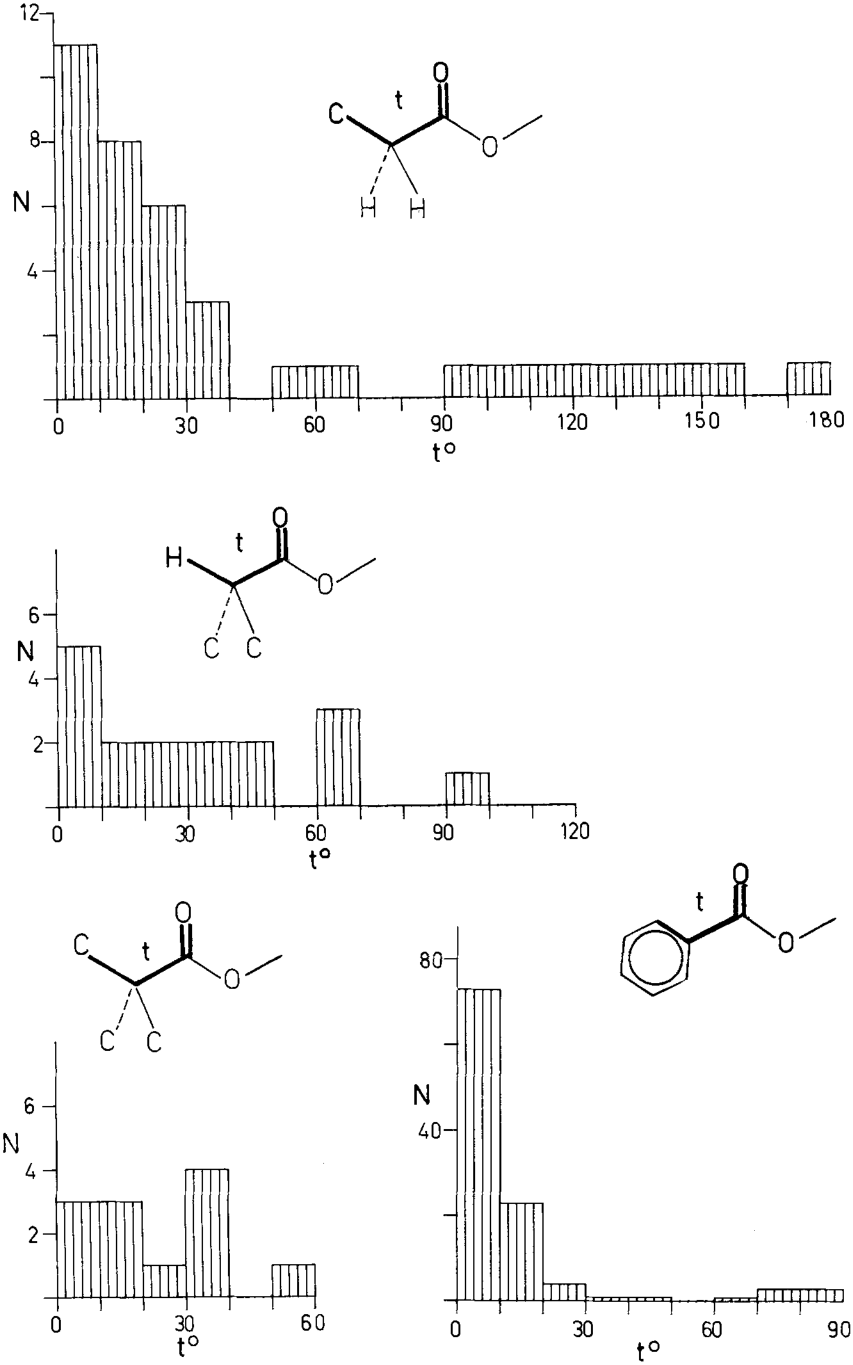

Fig. 4. *Histograms of O=C–C–C (or O=C–C–H) torsion angles* (absolute values) *for alkyl and aryl substituents at the carbonyl end of carboxylic esters* (Ranges of torsion angle as in *Fig. 2*)

lying closer to the plane of the ester group. This difference between esters of secondary alcohols on the one hand and those of primary and tertiary alcohols on the other is presumably connected with the difference in conformational preferences to which we alluded earlier *(Fig. 2)*. Even if we cannot see a simple explanation, the need for including appropriate terms in molecular mechanics calculations to allow for these kinds of correlation seems evident.

Conformational regularities at the other end of the ester group have also been looked for but the proportion of acetyl esters in our collection is so large that data for other kinds are not so extensive *(Fig. 4)*. In esters of the type $R-CH_2-COOX$ the $C(\alpha)$, $C(\beta)$-bond tends to be synperiplanar to the carbonyl bond, and in esters of the type Ar–COOX the aromatic system tends to lie close to the plane of the ester group. The few exceptions can be explained in terms of steric factors. For esters of the type RR′CH–COOX the few available examples indicate that the C,H-bond tends to be *syn* to the carbonyl bond. For esters of the type RR′R″C–COOX the available data are also somewhat meagre and do not seem to indicate any conformational preference whatsoever.

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