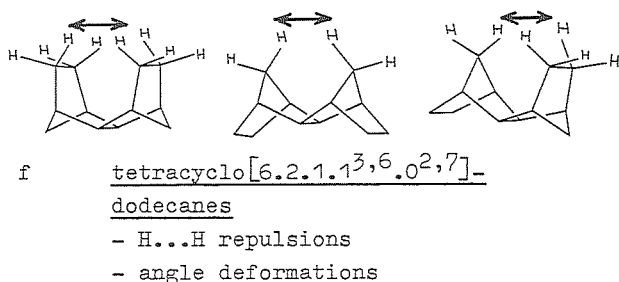
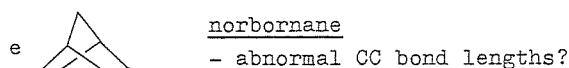
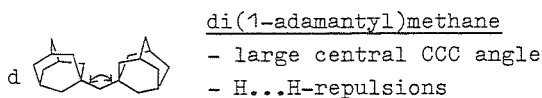
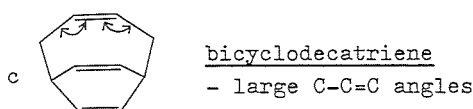
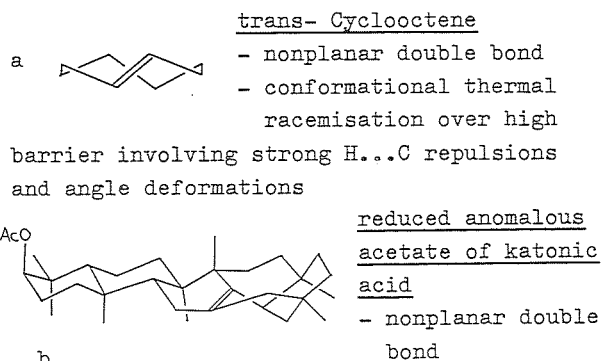


04.1-03 STRUCTURAL AND ENERGETICAL PROPERTIES OF SOME STRAINED HYDROCARBONS USEFUL FOR CALIBRATING MOLECULAR FORCE FIELDS. By Otto Ermer, Abteilung für Chemie, Ruhr-Universität, D463 Bochum, W-Germany.

The key properties relevant in the sense of the headline, which will be discussed for the various molecules, are summarised below. Published information on these systems may be found in: O. Ermer, Aspekte von Kraftfeldrechnungen, Wolfgang Baur Verlag, München 1981; compound d is described in: O. Ermer & C.D. Bödecker, Chem. Ber. 114, 652 (1981).

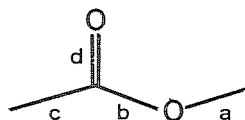


04.1-04 STRUCTURAL CHARACTERISTICS OF THE CARBOXYLIC ESTER GROUP. By W. B. Schweizer and J. D. Dunitz, Laboratorium für Organische Chemie, ETH-Zentrum, CH-8092 Zürich, Switzerland.

More than  $3 \times 10^3$  examples of carboxylic esters in the Cambridge Data File make it possible to examine the structural variability of this group. The ester group seldom deviates far from planarity, but its bond distances and angles 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).

	a	b	c	d
R. COOR	1.447(13)	1.340(14)	1.495(19)	1.195(7)
Ar. COOR	1.445(12)	1.343(14)	1.484(12)	1.199(6)
R. COOAr	1.402(13)	1.352(20)	1.497(16)	1.191(5)
$\gamma$ -lactones	1.462(8)	1.350(9)	1.515(13)	1.198(4)
$\delta$ -lactones	1.462(13)	1.337(8)	1.514(15)	1.204(7)
	ab	bd	bc	cd
R. COOR	117.4(1.6)	123.4(9)	111.2(1.0)	125.4(1.2)
Ar. COOR	117.2(1.6)	123.4(9)	111.6(8)	125.0(1.2)
R. COOAr	118.0(1.7)	122.7(1.1)	110.6(8)	126.7(1.6)
$\gamma$ -lactones	110.2(1.4)	121.7(9)	109.7(1.2)	128.6(8)
$\delta$ -lactones	122.9(2.9)	118.5(1.0)	118.4(1.7)	123.0(1.2)

Table: Standard dimensions based on structures with  $\sigma(\text{C-C}) \leq .005 \text{ \AA}$ .



There are pronounced conformational regularities for alkyl substituents at the O atom: esters of primary and tertiary alcohols usually have a C-O-C-C torsion angle close to  $180^\circ$ , whereas for secondary alcohols C-O-C-C torsion angles are usually close to  $\pm 120^\circ$ , i. e. the H-atom tends to eclipse the carbonyl bond, as first noted by Mathieson (Tetrahedron Letters, p. 4137, 1965). For tertiary alcohols the bond angle O-C-C (in plane) is about  $7^\circ$  smaller than the tetrahedral angle and the other two O-C-C angles are larger, i. e. the approximate threefold axis of the RR'R''C-grouping does not point along the C-O bond direction but deviates from it in a systematic way. Similar results have been reported for tertiary silyl nitronate esters (Colvin, Beck, Bastani, Seebach, Kai and Dunitz, Helv. Chim. Acta, 63, 697, 1980) and for the tert-butyl group itself (de Vos, Schreurs, van Duijneveldt and Kroon, Abstract 1-A-34, 6th ECM, Barcelona, 1980). In phenolic esters the plane of the phenyl group tends to be roughly perpendicular to the ester plane. Conformational regularities at the other end of the ester group are also observed. In esters R. CH<sub>2</sub>.COOX the C <sub>$\alpha$</sub> -C <sub>$\beta$</sub>  bond tends to be syn-planar to the C=O bond, and in Ar. COOX, the aromatic system tends to lie in the plane of the ester group. Both classes, however, show many exceptions, presumably due to steric factors. Esters of type RR'CH. COOX and RR'R''C. COOX do not show any pronounced conformational preferences.