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X-ray Structures of Three Products from the Electrohydrocyclodimerization of Dimethyl Benzene-1,2-diacrylate

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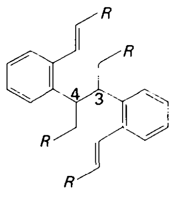
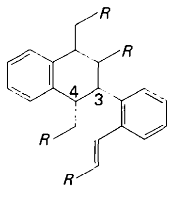
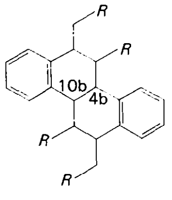
The crystal structures of the three molecular compounds



(I)



(II)

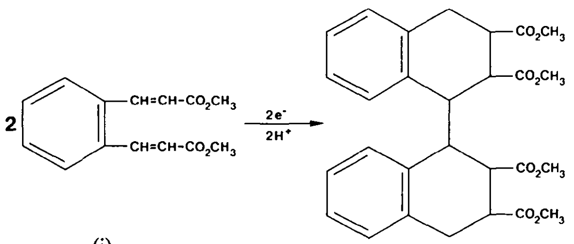


(III)

where $R = CO_2CH_3$, have been solved by direct methods from X-ray intensities collected with a four-circle diffractometer. All three compounds crystallize in space group $P\bar{1}$, $Z = 1$ (I) and 2 (II and III); the unit-cell constants are I: $a = 8\cdot378$ (1), $b = 9\cdot414$ (1), $c = 10\cdot251$ (1) Å, $\alpha = 66\cdot16$ (1), $\beta = 76\cdot66$ (1), $\gamma = 59\cdot69$ (1)°; II: $a = 8\cdot661$ (2), $b = 9\cdot553$ (2), $c = 18\cdot475$ (5) Å, $\alpha = 73\cdot50$ (2), $\beta = 79\cdot15$ (2), $\gamma = 64\cdot23$ (1)°; III: $a = 9\cdot274$ (1), $b = 10\cdot227$ (1), $c = 15\cdot564$ (2) Å, $\alpha = 71\cdot88$ (1), $\beta = 71\cdot52$ (1), $\gamma = 72\cdot94$ (1)°. The structures were refined to $R = 0\cdot043$ (I), $0\cdot045$ (II), and $0\cdot066$ (III). Molecule I is a *meso* form and has the centre of symmetry on the 3,4-bond. This gives a *trans* 3,4-arrangement. II and III crystallize as enantiomeric pairs. Both molecules have the *cis* arrangement at the bond corresponding to 3,4 in I (3,4 in II and 4b,10b in III). III has a $\sim C_2$ axis intersecting the 4b,10b-bond.

Introduction

On the evidence of NMR and MS data Andersson & Eberson (1976) suggested that the main product of the cathodic reduction of dimethyl benzene-1,2-diacrylate (i) is a single isomer of the hydrocyclodimer (ii), in spite of the fact that it can in principle exist in 20 isomeric forms (16 enantiomeric pairs and four *meso* forms).



(1)

(i) (ii)

In order to verify the proposed structure (ii) and to further elucidate the stereochemistry of the reaction (1) we have investigated the crystal structures of the three major products obtained in the cyclohydrodimerization (the main product and two other hydrodimers, the latter comprising 38% of the total amount of hydrodimer).

Experimental

Single crystals of the three products were prepared by Eberson (1977). All three had the composition $C_{28}H_{30}O_8$. I and III were picked from the same batch of single crystals, grown from methanol by slow evaporation at room temperature. The habit of I was tabular and of III acicular. Prismatic crystals of II were obtained when the solvent was changed to ethyl acetate. The three types of crystals were colourless or had a very faint yellow colour. III is the main product. In order to obtain a single crystal of this compound which was thick enough for intensity data collection, a needle several mm long had to be cut. Since the crystals easily cracked along the needle axis we never succeeded in mounting a specimen of the same quality as for I and II.

I, II, and III crystallize in the triclinic system. The unit-cell dimensions were determined from 35 (I), 49

(II) and 54 (III) θ values measured on a four-circle diffractometer (CAD-4) as described by Danielsson, Grenthe & Oskarsson (1976). Ni-filtered Cu $K\alpha$ radiation was used for I and III ($\lambda\alpha_1$ = 1·540562 Å) and Nb-filtered Mo $K\alpha$ radiation for II ($\lambda\alpha_1$ = 0·709300 Å).

The crystal data, the experimental parameters for the collection of intensity data, and some information about the refinements of the structures, are given in Table 1. Three standard reflexions were measured at regular intervals to check the electronic and crystal stability. The intensity variation was negligible for I and II but for III a decrease (total: 8%) linear with exposure time was observed. The intensities in the data set of III were compensated for this decrease. The values of I and $\sigma_c(I)$, where $\sigma_c(I)$ is based on counting statistics, were corrected for Lorentz, polarization and absorption effects, the latter by numerical integration.

The determination and refinement of the structures

Intensity statistics showed that all three structures were centrosymmetric (*i.e.* space group $P\bar{1}$). The non-H atoms were located from the intensity distribution using the program *MULTAN* (Germain, Main & Woolfson, 1971). After a few cycles of least-squares refinement (see below) the positions of the H atoms were calculated from geometrical considerations (CH and CH_2 groups) or located in difference maps (CH_3 groups). The H atoms bonded to C(30) in III were not located.

The atomic coordinates and thermal parameters were refined by a full-matrix least-squares technique (Table 1). The quantity minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = [\sigma_c^2(|F_o|^2)/4|F_o|^2 + C_1^2|F_o|^2 + C_2]^{-1}$. C_1 and C_2 were adjusted until the same value of $\langle w(|F_o| - |F_c|)^2\rangle$ was obtained in different $|F_o|$ and $\sin\theta$ intervals. With anisotropic thermal parameters assigned to all non-H atoms, the description of the structures of II and III requires more than 400 parameters. Therefore, only parts of these structures were refined at a time; in the last cycles the parameters of 33 non-H atoms were varied. The refinement of III converged to larger values of R, R_w, and S than the refinements of I and II. This was expected since the single crystal used for III was of low quality. This may also be the reason why some H atoms in III were refined to obviously wrong positions.

Table 1. *Crystal data at* 22 °C, *the collection and reduction of the intensity data sets, and the refinements of the structures*

Compound	I	II	III
Formula		$C_{28}H_{30}O_8$	
FW		494·54	
Space group		$P\bar{1}$ (triclinic)	
a (Å)	8·3778 (6)	8·6613 (16)	9·2736 (4)
b (Å)	9·4140 (6)	9·5525 (15)	10·2274 (9)
c (Å)	10·2507 (6)	18·4753 (54)	15·5643 (18)
α (°)	66·162 (5)	73·498 (17)	71·884 (7)
β (°)	76·663 (6)	79·146 (20)	71·523 (12)
γ (°)	59·694 (6)	64·234 (14)	72·937 (5)
V (Å^3)	638·07	1316·18	1299·22
Z	1	2	2
D_x (g cm^{-3})	1·287	1·248	1·264
Crystal size (mm)	0·25 × 0·25 × 0·10	0·15 × 0·10 × 0·16	0·34 × 0·10 × 0·04
Radiation	Cu $K\alpha$	Mo $K\alpha$	Cu $K\alpha$
$\Delta\omega$ (ω–2θ scan) (°)	0·6 + 0·3 tan θ	0·7 + 0·5 tan θ	0·6 + 0·3 tan θ
θ interval (°)	5–70	3–25	5–70
Minimum number of counts	1300	3000	1300
Maximum time of a scan (s)	180	180	180
μ (cm^{-1})	6·9	0·54	6·8
Range of transmission factor	0·79–0·96	0·99–1·00	0·86–0·97
Number of observed reflexions, m	1869	2074	2173
Number of unobserved reflexions [$I < 3\sigma_c(I)$]	551	2422	2732
Total number of parameters refined in the final cycle, n	224 (224)	299 (446)	299 (434)
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$*	0·043	0·045	0·066
$R_w = [\Sigma w(\Delta F)^2/\Sigma w\|F_o\|^2]^{1/2}$	0·057	0·058	0·086
$S = [\Sigma w(\Delta F)^2/(m - n)]$	1·20	1·05	2·07
C_1 (weighting function)	0·03	0·04	0·03
C_2 (weighting function)	0·03	0·02	0
$g \times 10^{-4}$ (extinction)	0·37 (5)	0·08 (2)	
Maximum correction on $\|F_o\|$	1·23	1·13	1·14

* $\Delta F = |F_o| - |F_c|$.

Table 2. *Atomic coordinates* ($\times 10^4$, H *atoms* $\times 10^3$) *with estimated standard deviations*

		I			II			III	
	x	*y*	*z*	*x*	*y*	*z*	*x*	*y*	*z*
C(1)	−2922 (3)	4717 (3)	5888 (2)	6906 (5)	4655 (5)	768 (2)	667 (6)	8240 (6)	4532 (4)
C(2)	−3680 (3)	4103 (3)	7206 (3)	6690 (5)	5970 (5)	1025 (2)	437 (6)	7737 (6)	5478 (4)
C(3)	−3064 (3)	2324 (3)	7890 (2)	5428 (5)	6464 (5)	1593 (2)	1492 (7)	7825 (6)	5914 (4)
C(4)	−1697 (3)	1167 (3)	7245 (2)	4396 (5)	5623 (4)	1919 (2)	2743 (6)	8428 (6)	5384 (4)
C(5)	−922 (2)	1746 (2)	5906 (2)	4616 (4)	4280 (4)	1676 (2)	2987 (6)	8936 (5)	4427 (3)
C(6)	−1536 (2)	3562 (2)	5219 (2)	5891 (4)	3796 (4)	1092 (2)	1953 (5)	8828 (5)	3985 (4)
C(7)	−744 (3)	4269 (2)	3825 (2)	6162 (4)	2386 (4)	821 (2)	2105 (5)	9348 (5)	2944 (3)
C(8)	−1679 (3)	5782 (3)	2820 (2)	6992 (5)	1987 (5)	183 (2)	2489 (7)	8094 (6)	2517 (4)
C(9)	−869 (3)	6496 (3)	1442 (2)	7120 (5)	511 (5)	17 (2)	2257 (7)	8437 (7)	1565 (4)
O(10)	−1732 (3)	7879 (2)	541 (2)	6577 (4)	−405 (3)	423 (2)	1494 (6)	9514 (5)	1197 (3)
O(11)	913 (2)	5434 (2)	1258 (2)	7957 (5)	312 (4)	−660 (2)	2953 (5)	7381 (5)	1149 (3)
C(12)	1808 (6)	6069 (5)	−62 (3)	8102 (17)	−1064 (11)	−894 (5)	2732 (21)	7548 (18)	233 (7)
C(13)	467 (2)	422 (2)	5192 (2)	3503 (4)	3347 (4)	2039 (2)	4265 (5)	9692 (5)	3860 (3)
C(14)	2148 (3)	−997 (2)	6110 (2)	1693 (4)	4299 (4)	2376 (2)	5807 (5)	8701 (5)	3468 (3)
C(15)	3200 (2)	−290 (2)	6436 (2)	769 (5)	5877 (5)	1858 (2)	6416 (5)	7706 (5)	4269 (4)
O(16)	3176 (2)	1105 (2)	5748 (2)	653 (3)	6087 (3)	1188 (1)	6969 (4)	8033 (4)	4752 (3)
O(17)	4244 (2)	−1443 (2)	7571 (2)	7 (3)	7045 (3)	2241 (1)	6206 (4)	6412 (4)	4428 (3)
C(18)	5425 (4)	−948 (4)	7926 (3)	−1025 (9)	8622 (6)	1807 (4)	6681 (10)	5401 (7)	5252 (5)
C(19)				707 (5)	523 (5)	3061 (2)	7652 (6)	11911 (6)	2047 (4)
C(20)				1566 (7)	−1110 (6)	3288 (2)	7226 (8)	13370 (6)	1755 (4)
C(21)				3316 (6)	−1805 (5)	3317 (2)	5677 (8)	14021 (6)	1881 (4)
C(22)				4228 (5)	−838 (5)	3112 (2)	4537 (7)	13226 (5)	2297 (4)
C(23)				3382 (5)	814 (4)	2888 (2)	4954 (6)	11765 (5)	2582 (3)
C(24)				1597 (5)	1521 (5)	2858 (2)	6522 (6)	11097 (5)	2463 (3)
C(25)				593 (5)	3319 (5)	2538 (2)	7073 (5)	9510 (5)	2763 (3)
C(26)				−1113 (5)	4089 (5)	2999 (2)	7791 (6)	8918 (5)	1883 (4)
C(27)				−973 (6)	4207 (5)	3769 (2)	8497 (12)	7401 (8)	2092 (6)
O(28)				310 (4)	3627 (4)	4096 (2)	8311 (14)	6646 (7)	1699 (5)
O(29)				−2497 (4)	5072 (5)	4064 (2)	9307 (6)	6913 (5)	2685 (5)
C(30)				−2607 (15)	5288 (18)	4833 (6)	9964 (13)	5346 (9)	2653 (14)
C(31)				4415 (4)	1842 (4)	2654 (2)	3734 (5)	10893 (5)	3077 (3)
C(32)				4741 (5)	2269 (5)	3340 (2)	3314 (5)	10293 (5)	2415 (3)
C(33)				6159 (5)	946 (5)	3793 (2)	2625 (7)	11532 (6)	1705 (4)
O(34)				7208 (4)	−248 (4)	3607 (2)	1438 (5)	12361 (4)	1887 (3)
O(35)				6196 (4)	1266 (4)	4450 (2)	3563 (5)	11594 (5)	855 (3)
C(36)				7584 (7)	98 (7)	4924 (3)	2953 (12)	12725 (13)	143 (6)
H(1)	−329 (3)	591 (3)	546 (3)	792 (5)	416 (5)	35 (2)	3 (5)	812 (4)	420 (3)
H(2)	−466 (3)	487 (3)	763 (3)	745 (4)	654 (4)	78 (2)	−53 (6)	731 (5)	582 (4)
H(3)	−353 (3)	188 (3)	881 (3)	529 (4)	739 (4)	179 (2)	135 (6)	731 (5)	661 (3)
H(4)	−124 (3)	−5 (3)	771 (2)	333 (5)	597 (4)	232 (2)	345 (5)	849 (5)	575 (3)
H(7)	56 (3)	361 (3)	363 (2)	558 (5)	165 (4)	112 (2)	103 (5)	990 (4)	288 (3)
H(8)	−340 (4)	650 (3)	290 (3)	770 (6)	259 (6)	−18 (3)	181 (6)	731 (5)	298 (3)
H(8)	–	–	–	–	–	–	332 (5)	762 (4)	252 (3)
H(12)	320 (6)	522 (5)	4 (4)	885 (15)	−97 (12)	−139 (6)	338 (13)	713 (12)	3 (8)
H(12)	164 (6)	719 (6)	−9 (5)	895 (8)	−191 (7)	−56 (4)	308 (15)	894 (13)	−30 (8)
H(12)	125 (5)	616 (5)	−78 (4)	715 (6)	−120 (5)	−86 (3)	179 (12)	802 (10)	25 (6)
H(13)	96 (2)	102 (2)	430 (2)	328 (4)	286 (4)	161 (2)	452 (5)	1007 (5)	424 (3)
H(14)	307 (3)	−186 (3)	560 (3)	180 (5)	452 (5)	284 (2)	554 (5)	810 (4)	307 (3)
H(14)	176 (3)	−173 (3)	700 (3)	–	–	–	–	–	–
H(18)	628 (5)	−196 (4)	851 (4)	−41 (6)	894 (5)	136 (3)	344 (9)	553 (9)	487 (5)
H(18)	606 (6)	−38 (6)	706 (5)	−158 (7)	928 (7)	218 (4)	395 (16)	423 (12)	393 (9)
H(18)	457 (5)	−9 (4)	839 (3)	−196 (6)	865 (5)	167 (3)	314 (12)	463 (11)	479 (8)
H(19)				−59 (5)	109 (4)	299 (2)	874 (7)	1147 (6)	185 (4)
H(20)				92 (5)	−168 (5)	341 (2)	807 (8)	1391 (7)	142 (4)
H(21)				399 (5)	−284 (4)	344 (2)	540 (6)	1502 (5)	165 (3)
H(22)				558 (5)	−138 (4)	316 (2)	333 (6)	1368 (6)	240 (4)
H(25)				34 (6)	343 (5)	202 (2)	790 (4)	928 (4)	309 (2)
H(26)				−179 (6)	530 (5)	274 (2)	875 (8)	940 (7)	147 (5)
H(26)				−180 (6)	348 (6)	308 (3)	695 (8)	906 (6)	157 (4)
H(30)				−405 (5)	603 (5)	506 (2)	–	–	–
H(30)				−230 (13)	410 (12)	514 (6)	–	–	–
H(30)				−225 (4)	588 (3)	465 (2)	–	–	–
H(31)				558 (4)	113 (4)	242 (2)	286 (5)	1149 (4)	334 (3)
H(32)				369 (5)	249 (4)	368 (2)	415 (11)	1235 (9)	941 (6)
H(32)				516 (5)	332 (5)	316 (2)	–	–	–
H(36)				726 (5)	50 (4)	542 (2)	351 (23)	1261 (20)	−18 (12)
H(36)				903 (5)	16 (5)	467 (2)	198 (10)	1255 (8)	22 (5)
H(36)				749 (6)	−81 (6)	496 (3)	320 (12)	1348 (10)	32 (7)

A correction for isotropic extinction (Zachariasen, 1967) was applied to $|F_o|$ in all three structures. The scattering factors were taken from Doyle & Turner (1968) (for C and O) and from Stewart, Davidson & Simpson (1965) (for H). Table 2 gives the atomic coordinates for I, II and III.*

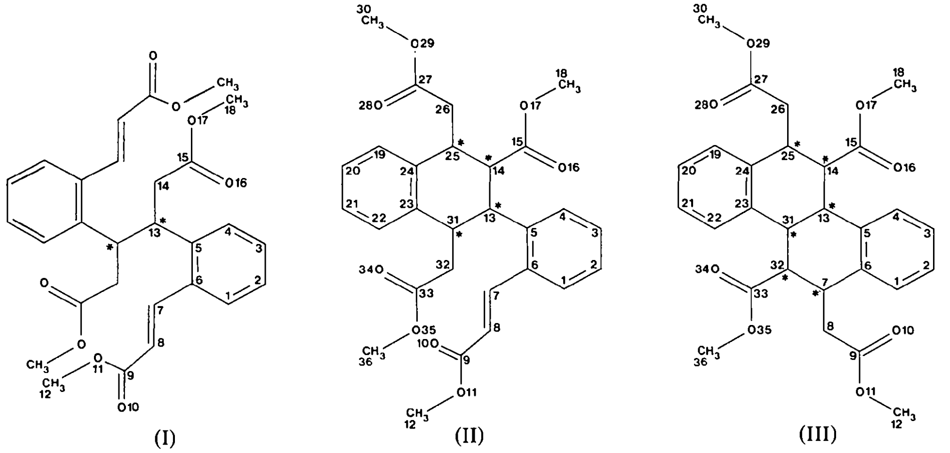
Description of the structures

None of I, II, and III has the proposed structure (ii) of equation (1). The connectivity in each molecule is given in Fig. 1 together with the atomic numbering. Systematic names of the three compounds are I: dimethyl *meso*-3,4-bis[2-(2-methoxycarbonylvinyl)phenyl]-1,6-hexanoate, II: trimethyl 2-carboxylato-*trans*-3-[2-(2-methoxycarbonylvinyl)phenyl]-1,2,3,4-tetrahydronaphthalene-*cis*-1,4-diacetate, and III: tetramethyl *cis*-5,11-dicarboxylato-*cis*-4b,5,6,10b,11,12-hexahydrochrysene-*cis*-6,12-diacetate (the numbering used here is according to IUPAC rules, not according to Fig. 1). Molecule I has centrosymmetrically related centres of chirality marked with asterisks in Fig. 1. II and III crystallize as enantiomeric pairs; II has four chirality centres and III has six.

Fig. 2 shows stereoviews of the three molecules; III is stripped of its H atoms. The molecular packing is shown in Fig. 3. The shape of I and II obviously facilitates an efficient van der Waals packing resulting in well developed single crystals. The cracking of the acicular crystals of III along the needle axis *a* is understood from its molecular packing. The molecules do not fit well in the *b* axis direction leaving much empty space and weak van der Waals bonds across the planes $y = \frac{1}{2}$.

Table 3 gives bond lengths, bond angles and torsion angles involving the non-H atoms. The geometries of the three molecules are as expected from Fig. 1. In molecule II bond lengths and angles around C(7) and C(32) are different from those around C(14) and C(25) due to the formation of the bond C(14)–C(25). Besides the low quality of the crystal of III another reason for the large thermal parameters of C(27)–C(30) in the molecule may be a disorder of this methoxycarbonyl group, *cf.* the thermal vibration ellipsoids in Fig. 2. The positions given for its atoms (with occupancy 1) result in unusual values of some bond lengths and angles. These are marked with asterisks in Table 3(*a*) and (*b*).

The signs given in Table 3(*c*) for the torsion angles in II should be reversed when I, II and III are compared since the coordinates of opposite members of the two enantiomeric pairs of II and III are given in Table 2. The arrangement of the central part of the molecules about the bond C(13)–C(13′) in I and C(13)–C(31) in II and III is *trans* in I as required by the centre of symmetry between C(13) and C(13′) and *cis* in II and III. Following Duax & Norton (1975) we have used the asymmetry parameters ΔC_s and ΔC_2 to identify the most ideal symmetries of the partly hydrogenated rings from their endocyclic torsion angles. Table 4 gives some ΔC values and the average endocyclic dihedral angles for the three rings, one in II and two in III. They are all very distorted from the ideal conformations of a six-membered ring, but the best description based on Table 4 is (i) a sofa for the ring in II with C(13) out of the plane; (ii) a half-chair for the ring connected to C(23)–C(24) in III with C(13) and C(31) out of the plane; and (iii) a sofa for the other ring in III with C(31) out of the plane. The expected conformation of the partially hydrogenated ring in tetralin is a half-chair since the C atoms (1) and (4) [C(25) and C(31) or C(7) and C(13)] should lie in the plane of the aromatic ring (Drehfahl & Ponsold, 1958; Drehfahl & Martin, 1960; Godfrey & Waters, 1973). Table 5 lists the deviations from the relevant least-squares planes in II and III.



(I) (II) (III)

Fig. 1. Molecular skeletons of the compounds I, II, and III and the numbering of the atoms.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33601 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

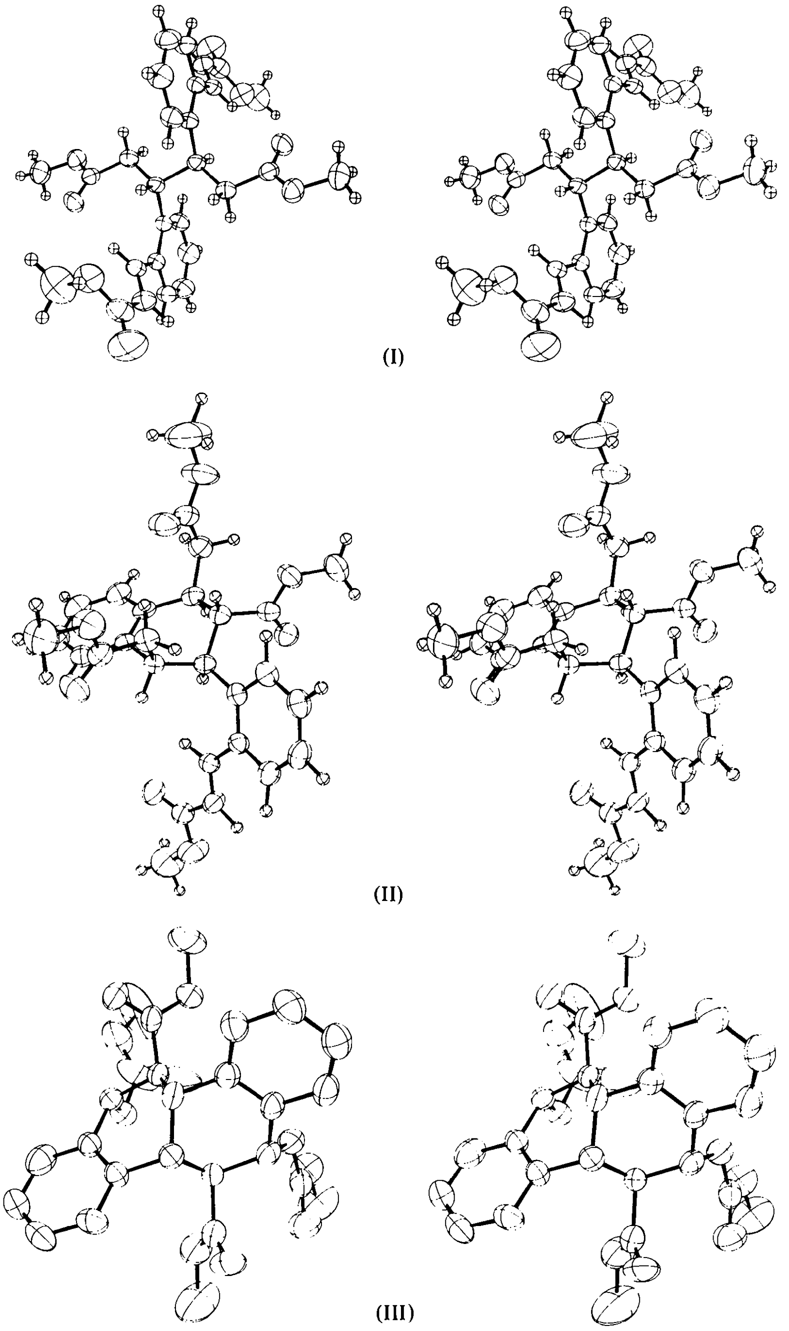

Fig. 2. Stereoscopic pairs of drawings of the three molecules. III is stripped of its H atoms. The thermal ellipsoids of the non-H atoms are scaled to include 50% probability.

The methoxycarbonylvinyl chain is planar in both I and II as shown by Tables 3(*c*) and 5. In I the chain is oriented clinal to the aromatic ring and in II periplanar; the angle difference between I and II is 14·0°. The C(9)–O(10) carbonyl bond is synplanar to the C(7)–C(8) double bond in II as it is in most α,β-unsaturated carboxyl esters and in acrylic acid (Leiserowitz, 1976). In contrast to this, I exhibits the antiplanar conformation. The methoxycarbonyl groups [C(8)–C(12), C(14)–C(18), C(26)–C(30), and C(32)–C(36)] are planar in the three structures. III has almost twofold rotation symmetry with the pseudo-axis intersecting the C(13)–C(31) bond [Table 3(*c*)]. The main deviation is that the two methyl acetate substituents have different orientations relative to the hexahydrochrysene nucleus of the molecule. Like the

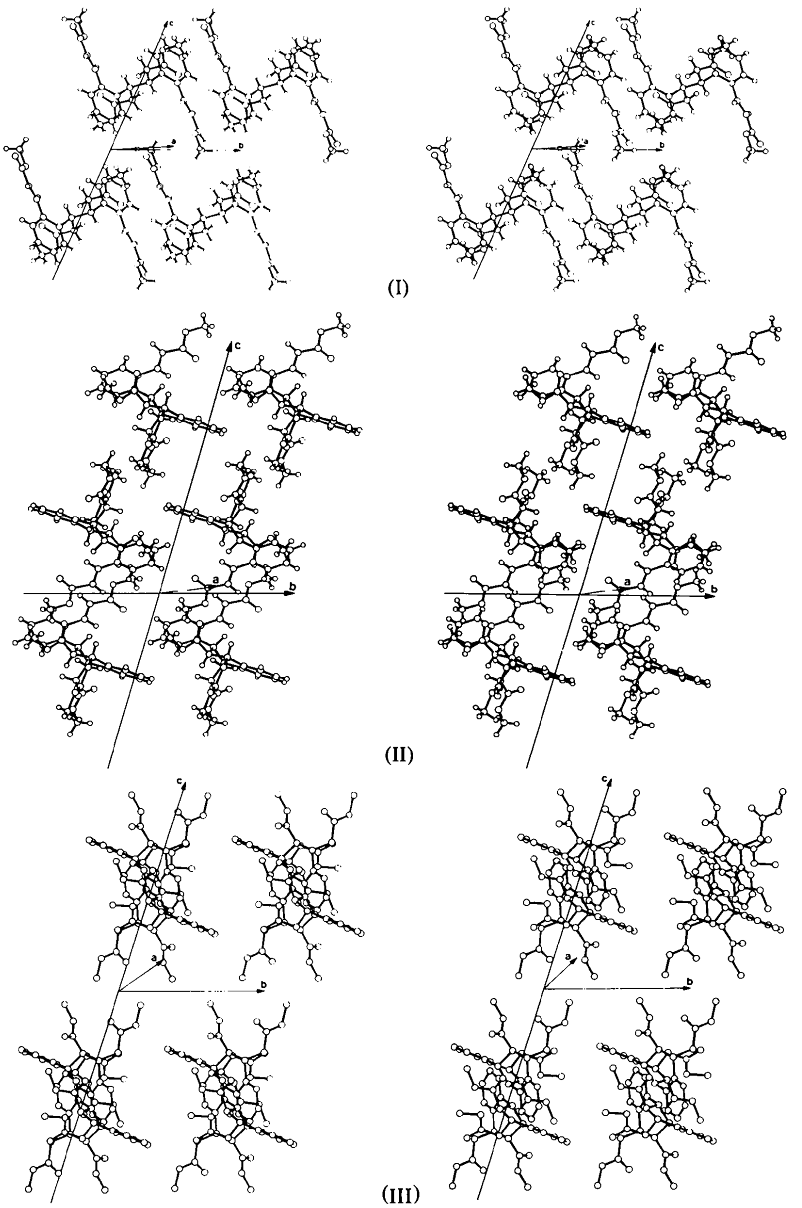

Fig. 3. Stereoscopic pairs of drawings of the molecular packing in compounds I, II, and III.

Table 3. *Bond distances* (Å), *bond angles* (°) *and torsion angles* (°) *with estimated standard deviations*

In I the atoms C(23), C(31) and C(32) are centrosymmetrically related to C(5), C(13) and C(14), respectively

		I	II		III	
(*a*) Bond distances						
C(1)–C(2)	C(19)–C(20)	1·381 (3)	1·394 (4)	1·379 (7)	1·368 (8)	1·391 (8)
C(2)–C(3)	C(20)–C(21)	1·381 (3)	1·385 (6)	1·370 (7)	1·392 (8)	1·374 (9)
C(3)–C(4)	C(21)–C(22)	1·381 (3)	1·397 (5)	1·394 (6)	1·379 (8)	1·393 (8)
C(4)–C(5)	C(22)–C(23)	1·395 (3)	1·401 (5)	1·392 (5)	1·385 (7)	1·392 (7)
C(5)–C(6)	C(23)–C(24)	1·411 (2)	1·410 (5)	1·398 (5)	1·390 (7)	1·393 (7)
C(6)–C(1)	C(24)–C(19)	1·400 (3)	1·398 (5)	1·404 (6)	1·403 (7)	1·398 (8)
C(6)–C(7)	C(24)–C(25)	1·471 (2)	1·478 (5)	1·541 (5)	1·514 (7)	1·518 (7)
C(7)–C(8)	C(25)–C(26)	1·328 (3)	1·324 (5)	1·544 (5)	1·525 (7)	1·545 (7)
C(8)–C(9)	C(26)–C(27)	1·469 (3)	1·480 (6)	1·491 (6)	1·483 (8)	1·472 (9)
C(9)–O(10)	C(27)–O(28)	1·207 (3)	1·183 (5)	1·197 (5)	1·203 (8)	1·200 (11)

Table 3 (*cont.*)

		I	II		III	
C(9)–O(11)	C(27)–O(29)	1·334 (3)	1·342 (5)	1·326 (6)	1·328 (8)	
O(11)–C(12)	O(29)–C(30)	1·442 (4)	1·446 (10)	1·473 (12)	1·456 (12)	*1·549 (11)
C(5)–C(13)	C(23)–C(31)	1·524 (2)	1·529 (5)	1·526 (5)	1·494 (7)	1·510 (7)
C(13)–C(14)	C(31)–C(32)	1·533 (2)	1·545 (5)	1·543 (5)	1·557 (6)	1·543 (7)
C(14)–C(15)	C(32)–C(33)	1·497 (2)	1·500 (5)	1·497 (5)	1·493 (7)	1·528 (7)
C(15)–O(16)	C(33)–O(34)	1·205 (2)	1·212 (5)	1·203 (5)	1·200 (6)	1·190 (6)
C(15)–O(17)	C(33)–O(35)	1·337 (2)	1·347 (5)	1·341 (5)	1·330 (6)	1·327 (7)
O(17)–C(18)	O(35)–C(36)	1·449 (3)	1·457 (3)	1·461 (6)	1·474 (8)	1·450 (11)
C(7)–C(32)	C(14)–C(25)	–	–	1·543 (5)	1·558 (7)	1·568 (7)
C(13)–C(31)		1·556 (3)	1·550 (5)		1·526 (7)	
(*b*) Bond angles						
C(2)–C(1)–C(6)	C(20)–C(19)–C(24)	121·1 (2)	120·6 (4)	121·0 (4)	121·8 (5)	120·8 (5)
C(1)–C(2)–C(3)	C(19)–C(20)–C(21)	120·0 (2)	120·0 (4)	120·8 (4)	119·4 (5)	119·6 (6)
C(2)–C(3)–C(4)	C(20)–C(21)–C(22)	119·7 (2)	120·0 (4)	119·4 (4)	119·3 (5)	120·3 (5)
C(3)–C(4)–C(5)	C(21)–C(22)–C(23)	121·7 (2)	120·8 (3)	120·9 (4)	121·7 (5)	120·4 (5)
C(4)–C(5)–C(6)	C(22)–C(23)–C(24)	118·4 (2)	118·8 (3)	119·9 (3)	119·3 (5)	119·7 (5)
C(1)–C(6)–C(5)	C(19)–C(24)–C(23)	119·1 (2)	119·8 (3)	118·2 (4)	118·6 (5)	119·2 (4)
C(1)–C(6)–C(7)	C(19)–C(24)–C(25)	119·3 (2)	119·8 (3)	118·6 (3)	117·6 (4)	117·9 (4)
C(5)–C(6)–C(7)	C(23)–C(24)–C(25)	121·6 (2)	120·4 (3)	122·9 (3)	123·8 (4)	122·9 (4)
C(6)–C(7)–C(8)	C(24)–C(25)–C(26)	124·8 (2)	127·8 (3)	114·3 (3)	109·5 (4)	108·8 (4)
C(7)–C(8)–C(9)	C(25)–C(26)–C(27)	124·4 (2)	119·3 (4)	116·5 (3)	115·4 (5)	113·1 (5)
C(8)–C(9)–O(10)	C(26)–C(27)–O(28)	123·8 (2)	125·5 (4)	126·6 (4)	125·9 (6)	*120·2 (8)
C(8)–C(9)–O(11)	C(26)–C(27)–O(29)	113·3 (2)	111·4 (3)	110·6 (4)	112·1 (5)	*119·0 (7)
O(10)–C(9)–O(11)	O(28)–C(27)–O(29)	122·9 (2)	123·0 (4)	122·8 (4)	122·0 (6)	120·8 (8)
C(9)–O(11)–C(12)	C(27)–O(29)–C(30)	116·3 (2)	116·3 (5)	118·1 (6)	117·6 (8)	*104·3 (9)
C(4)–C(5)–C(13)	C(22)–C(23)–C(31)	119·4 (2)	120·8 (3)	119·8 (3)	121·9 (4)	121·1 (5)
C(6)–C(5)–C(13)	C(24)–C(23)–C(31)	122·0 (1)	120·4 (3)	120·3 (3)	118·7 (4)	119·1 (4)
C(5)–C(13)–C(14)	C(23)–C(31)–C(32)	112·2 (1)	116·4 (3)	111·9 (3)	113·4 (4)	113·0 (4)
C(5)–C(13)–C(31)	C(13)–C(31)–C(23)	111·1 (2)	112·6 (3)	109·7 (3)	110·7 (4)	110·5 (4)
C(14)–C(13)–C(31)	C(13)–C(31)–C(32)	110·5 (2)	108·2 (3)	112·2 (3)	111·0 (4)	109·7 (4)
C(13)–C(14)–C(15)	C(31)–C(32)–C(33)	113·6 (1)	112·7 (3)	113·9 (3)	108·6 (4)	108·1 (4)
C(14)–C(15)–O(16)	C(32)–C(33)–O(34)	125·2 (2)	125·4 (4)	126·7 (4)	124·6 (4)	125·0 (5)
C(14)–C(15)–O(17)	C(32)–C(33)–O(35)	111·0 (2)	111·0 (3)	111·5 (3)	112·5 (4)	110·8 (5)
O(16)–C(15)–O(17)	O(34)–C(33)–O(35)	123·7 (2)	123·6 (4)	121·8 (4)	122·9 (5)	124·2 (5)
C(15)–O(17)–C(18)	C(33)–O(35)–C(36)	115·9 (2)	116·3 (2)	116·6 (4)	115·2 (4)	113·5 (5)
C(6)–C(7)–C(32)	C(14)–C(25)–C(24)	–	–	113·6 (3)	114·7 (4)	115·4 (4)
C(7)–C(32)–C(31)	C(13)–C(14)–C(25)	–	–	109·7 (3)	112·3 (4)	113·4 (4)
C(7)–C(32)–C(33)	C(15)–C(14)–C(25)	–	–	108·2 (3)	108·9 (4)	110·7 (4)
C(8)–C(7)–C(32)	C(14)–C(25)–C(26)	–	–	113·6 (3)	110·1 (4)	110·6 (4)
(*c*) Torsion angles						
C(5)–C(6)–C(7)–C(32)	C(23)–C(24)–C(25)–C(14)	–	–	−9·4 (5)	−11·9 (7)	−17·2 (7)
C(6)–C(7)–C(32)–C(31)	C(24)–C(25)–C(14)–C(13)	–	–	39·4 (4)	−18·0 (6)	−9·0 (6)
C(7)–C(32)–C(31)–C(13)	C(25)–C(14)–C(13)–C(31)	–	–	−65·9 (4)	53·8 (5)	46·7 (6)
C(32)–C(31)–C(13)–C(5)	C(14)–C(13)–C(31)–C(23)	−176·3 (2)	65·2 (4)	60·2 (4)	−61·7 (5)	−60·2 (5)
C(31)–C(13)–C(5)–C(6)	C(13)–C(31)–C(23)–C(24)	−110·2	81·7 (4)	−30·2 (5)	32·9 (6)	35·6 (6)
C(7)–C(6)–C(5)–C(13)	C(25)–C(24)–C(23)–C(31)	−5·6 (3)	0·3 (5)	4·8 (6)	4·3 (8)	
C(5)–C(13)–C(31)–C(23)		180	−169·8 (3)		173·0 (4)	
C(14)–C(13)–C(31)–C(32)		180	−64·8 (4)		65·1 (5)	
C(1)–C(6)–C(7)–C(8)	C(19)–C(24)–C(25)–C(26)	−34·3 (3)	−16·9 (6)	47·5 (5)	−69·4 (6)	−72·0 (6)
C(5)–C(6)–C(7)–C(8)	C(23)–C(24)–C(25)–C(26)	146·3 (2)	163·1 (4)	−138·9 (4)	112·4 (6)	107·8 (6)
C(6)–C(7)–C(8)–C(9)	C(24)–C(25)–C(26)–C(27)	178·7 (2)	179·9 (4)	68·1 (5)	164·2 (5)	174·5 (6)
C(32)–C(7)–C(8)–C(9)	C(14)–C(25)–C(26)–C(27)	–	–	−62·5 (5)	−68·8 (6)	−57·7 (7)
C(7)–C(8)–C(9)–O(10)	C(25)–C(26)–C(27)–O(28)	−179·5 (3)	−2·3 (7)	−8·0 (7)	−17·7 (1·0)	137·9 (9)
C(7)–C(8)–C(9)–O(11)	C(25)–C(26)–C(27)–O(29)	2·7 (4)	178·2 (4)	171·6 (4)	164·8 (5)	−42·6 (1·0)
C(8)–C(9)–O(11)–C(12)	C(26)–C(27)–O(29)–C(30)	−178·8 (3)	−177·7 (6)	178·8 (7)	176·2 (9)	−175·0 (9)
O(10)–C(9)–O(11)–C(12)	O(28)–C(27)–O(29)–C(30)	3·4 (4)	2·8 (8)	−1·6 (9)	−1·5 (1·2)	4·5 (1·3)
C(4)–C(5)–C(13)–C(14)	C(22)–C(23)–C(31)–C(32)	−58·2 (2)	27·7 (5)	−86·7 (4)	91·9 (6)	96·4 (6)
C(5)–C(13)–C(14)–C(15)	C(23)–C(31)–C(32)–C(33)	−59·6 (2)	45·6 (5)	78·5 (4)	−64·5 (5)	−62·2 (6)
C(31)–C(13)–C(14)–C(15)	C(13)–C(31)–C(32)–C(33)	175·9 (2)	173·5 (3)	−157·7 (3)	170·1 (4)	174·0 (4)
C(13)–C(14)–C(15)–O(16)	C(31)–C(32)–C(33)–O(34)	−22·4 (3)	47·3 (6)	13·6 (6)	−71·1 (7)	−64·7 (7)
C(13)–C(14)–C(15)–O(17)	C(31)–C(32)–C(33)–O(35)	160·1 (2)	103·2 (4)	−169·2 (3)	105·5 (5)	112·9 (5)
C(25)–C(14)–C(15)–O(16)	C(7)–C(32)–C(33)–O(34)	–	−74·2 (5)	–	54·0 (7)	57·6 (8)
C(25)–C(14)–C(15)–O(17)	C(7)–C(32)–C(33)–O(35)	–	103·2 (4)	–	−129·3 (5)	−124·9 (5)
C(14)–C(15)–O(17)–C(18)	C(32)–C(33)–O(35)–C(36)	175·9 (2)	−176·3 (4)	−176·9 (4)	−175·8 (5)	178·3 (6)
O(16)–C(15)–O(17)–C(18)	O(34)–C(33)–O(35)–C(36)	−1·7 (3)	1·2 (6)	0·5 (6)	0·9 (8)	−4·2 (1·0)

Table 4. *Asymmetry parameters* (°) *and average endocyclic dihedral angles* (°) *for the cyclohexene rings*

Asymmetry parameter notation, ΔC_s and ΔC_2, from Duax & Norton (1975).

Ring	Most ideal symmetry	Next highest symmetry	Parameter for symmetry orthogonal to most ideal symmetry	Average endocyclic dihedral angle
II: 13–14–25–24–23–31	$\Delta C_s(13) = 6·8$	$\Delta C_2(13,14) = 20·8$	$\Delta C_2(14,25) = 56·0$	35·0
III: 13–14–25–24–23–31	$\Delta C_2(13,31) = 11·8$	$\Delta C_s(13) = 19·0$	$\Delta C_2(14) = 44·7$	28·7
III: 5–6–7–32–31–13	$\Delta C_s(6) = 10·6$	$\Delta C_2(6,7) = 21·9$	$\Delta C_s(5,13) = 29·6$	25·0

Table 5. *Deviations* (Å) *from the least-squares planes through the ring systems in* I–III *and through the* C(7)–C(12) *chain in* I *and* II

Plane 1	Plane 2	I	II		III		Plane 3	I	II
C(1)	C(19)	0·001	−0·008	0·026	0·029	0·011	C(7)	0·010	−0·029
C(2)	C(20)	−0·004	0·009	−0·004	0·027	0·012	C(8)	−0·006	0·013
C(3)	C(21)	0·001	−0·003	−0·026	−0·008	0·000	C(9)	0·006	0·012
C(4)	C(22)	0·004	−0·003	−0·019	−0·030	−0·012	C(10)	0·000	0·015
C(5)	C(23)	−0·008	0·004	0·024	−0·031	−0·026	C(11)	−0·024	0·020
C(6)	C(24)	0·005	0·001	0·046	−0·021	−0·006	C(12)	0·014	−0·032
C(7)	C(25)	–	–	−0·054	−0·021	−0·008	∠ plane 1–3	33·4 (5)°	19·4 (1·0)°
C(13)	C(31)	–	–	0·007	0·056	0·030			
*C(31)	*C(13)	–	–	−0·718	0·909	0·924			
*C(32)	*C(14)	–	–	0·050	0·258	0·385			

differences in bond distances and angles, this difference in torsion angles may partly be an effect of the suspected disorder of the C(26)—C(30) group.

Discussion

The formation of II and III cannot occur *via* the *meso* form I since this molecule has a *trans* arrangement at the C(13)—C(13′) bond while II and III are *cis* at the corresponding C(13)—C(31) bonds. Instead we have to invoke the racemic form of I. The mechanism of the cyclohydrodimerization can then be pictured as an initial dimerization of the anion radical of dimethyl benzene-1,2-diacrylate [compound (i) of equation (1)] by coupling through the β-positions to give a mixture of about $\frac{1}{3}$ *meso* form [the *R*—*S* stereoisomer of the C(13)—C(13′) arrangement] and about $\frac{2}{3}$ racemic form (the *R*—*R* and *S*—*S* isomers) of the dimeric anion [(i)—(i)]$^{2-}$. Competing protonation and cyclization of the three stereoisomers determine the hydrodimer product composition. Thus, the formation of the precursor dianion is the step that ultimately controls the stereochemistry of II and III (Eberson, 1977).

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