Tabelle 3. *Atomabstände*

(*a*) Nächste Nachbarn

Abstände im Ikosaeder	zwischen 1,78 und 1,91 Å	Mittelwert 1,83 Å
Abstände im Inneren System	zwischen 1,69 und 1,99	Mittelwert 1,80
Interikosaederabstände	zwischen 1,61 und 1,86	Mittelwert 1,72
Abstände in der Gesamtstruktur	zwischen 1,61 und 1,99	Mittelwert 1,80

(*b*) Individuelle Atomabstände
(Die Nummern beziehen sich auf Fig. 1, Fig. 2 und Tabelle 2. Hinter den Atomen, die mit Buchstaben bezeichnet sind, steht die Atomart in Klammern).

Maximaler und minimaler Abstand im Ikosaeder in 000				
	2–*a*(2):	1,78 Å	1–*b*(2):	1,81 Å
Maximaler und minimaler Abstand im Ikosaeder in $\frac{1}{2}$00				
	6–*c*(6):	1,80 Å	5–*d*(5):	1,91 Å
Maximaler und minimaler Abstand im inneren Ikosaedersystem				
	15–11:	1,69 Å	11–*e*(11):	1,99 Å
Wichtige Interikosaederabstände	1—3:	1,69 Å	*d*(5)–*f*(5):	1,86 Å
	4–10:	1,72	2–7:	1,61

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The Crystal Structure of Tricyclo[4,3,1,1^{3,8}]undecane-4,5-dione

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The yellow crystals of tricyclo[4,3,1,1^{3,8}]undecane-4,5-dione are orthorhombic with space group $P2_12_12_1$ and $Z=4$. Unit-cell dimensions at room temperature are $a=13{\cdot}52$, $b=6{\cdot}519$, $c=10{\cdot}11$ Å. Three-dimensional intensity data were collected with an automatic single-crystal diffractometer. The structure was solved using an automatic Patterson search method, assuming the conformation of a part of the molecule to be known. It was refined by the method of least squares to an R_w value of 3·7%. Deviations from molecular symmetry C_2 are small, but significant. The dihedral angle in the 4,5-dicarbonyl chromophore is 11·9°.

Introduction

The compound $C_{11}H_{14}O_2$ (m.p. = 287 °C) was synthesized at the Philips Duphar Research Laboratories at Weesp, the Netherlands by oxidation of tricyclo-[4,3,1,1^{3,8}]undecane-4-one with SeO_2 in dioxane (Schlatmann, Korsloot & Schut, 1970). The ultraviolet absorption spectrum showed a $\lambda_{\max}$ of 418 nm, indicating a much flatter configuration of the dicarbonyl system than is normally found in such a system in seven-membered rings (Leonard & Mader, 1950). To remove this discrepancy we determined the crystal structure.

The molecule is expected to have a twofold axis. The latter is not present in the space group. It is interesting to study the deviations from this molecular symmetry in the refined crystal structure.

Experimental

A single crystal was ground to an almost spherical shape with a radius of 0·2 mm. Lattice constants and X-ray intensities were measured at room temperature, using the Philips automatic single-crystal diffractometer PAILRED, with crystal-monochromatized Cu *Kα* radiation ($\lambda=1{\cdot}54178$ Å). The measured intensities were corrected for Lorentz polarization and absorption effects. The 1840 reflexions, confined within a sphere with a radius corresponding to 0·81 Å, were collected in zero and 14 higher levels about [111]. In the structure

Table 1. *Positional coordinates*

Estimated standard deviations are given in brackets.

	x	y	z
C(1)	0·11636 (16)	0·42683 (32)	0·40231 (19)
C(2)	0·18362 (15)	0·46662 (33)	0·52183 (22)
C(3)	0·19986 (13)	0·27905 (34)	0·61225 (20)
C(4)	0·11792 (15)	0·25163 (32)	0·71120 (17)
C(5)	0·01020 (14)	0·23077 (30)	0·66185 (17)
C(6)	−0·01120 (13)	0·19796 (31)	0·51751 (18)
C(7)	0·04129 (15)	0·01208 (31)	0·45713 (19)
C(8)	0·14842 (14)	0·05327 (32)	0·41581 (19)
C(9)	0·15381 (16)	0·24031 (37)	0·32637 (20)
C(10)	0·00823 (15)	0·39607 (36)	0·43957 (21)
C(11)	0·21738 (15)	0·07936 (34)	0·53357 (23)
O(12)	0·13156 (12)	0·24592 (32)	0·82888 (14)
O(13)	−0·05452 (11)	0·24401 (29)	0·74349 (13)
H(1)	0·1209 (17)	0·5496 (37)	0·3383 (21)
H(2)	0·1592 (17)	0·5926 (40)	0·5792 (23)
H(2)	0·2534 (18)	0·5049 (40)	0·4886 (26)
H(3)	0·2616 (16)	0·3092 (35)	0·6712 (23)
H(6)	−0·0858 (16)	0·1622 (38)	0·5179 (21)
H(7)	0·0021 (15)	−0·0283 (34)	0·3769 (23)
H(7)	0·0371 (18)	−0·1057 (39)	0·5211 (22)
H(8)	0·1710 (16)	−0·0696 (39)	0·3643 (23)
H(9)	0·2297 (18)	0·2710 (39)	0·3003 (22)
H(9)	0·1132 (18)	0·2227 (35)	0·2399 (19)
H(10)	−0·0170 (16)	0·5272 (35)	0·4915 (25)
H(10)	−0·0292 (18)	0·3920 (42)	0·3537 (24)
H(11)	0·2863 (18)	0·0874 (41)	0·4950 (25)
H(11)	0·2091 (17)	−0·0498 (40)	0·5977 (25)

determination and subsequent refinement we used the set of 1032 independent reflexions that could be derived from the measured data.

The crystals are orthorhombic with space group $P2_12_12_1$ and $Z=4$; $a=13·52\pm0·01$, $b=6·519\pm0·003$, $c=10·11\pm0·01$ Å.

Structure determination

Sinec the Patterson-search method employed has been described in detail (Braun, Hornstra & Leenhouts, 1969) only a short survey will be given here.

Assuming the conformation of the molecular fragment C(1), C(2), C(3), C(6), C(7), C(8), C(9), C(10) and C(11) to be known, we used this as a search model, with dimensions derived from a Dreiding model of the molecule. A Patterson search yields a small number of possible orientations of this model in the unit cell. A second search is done to determine a small number of possible positions, with respect to the symmetry elements, for each of these oriented models. The third step, applied to all possibilities left, is a combined optimization in Patterson space of the 6 parameters (3 angles and 3 vector components) defining such a possibility. The correct solution emerges from the mass, showing the best fit to the Patterson function. The automatic procedure performing the three linked steps produced this result in 15 minutes on a CD 3600 computer.

The atoms not incorporated in the model were also found one after the other by an automatic Patterson search. Positions in the neighbourhood of the located model, possibly occupied by new atoms, were calculated from stereochemical knowledge. That position which fitted the Patterson function best was taken as the site of a new atom. This atom and its symmetry-related ones were added to the known part of the structure and the process was repeated until the molecule was complete. This computer program needed another 5 minutes to complete the structure. The atomic parameters obtained were sufficiently accurate to start a converging least-squares refinement.

The programs, written in FORTRAN 63, may be obtained from the authors on request.

Refinement

The weighting scheme used in the least-squares refinement has been described elsewhere (Braun, Hornstra & Leenhouts, 1970). The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The non-hydrogen atoms were refined in a 9 × 9 block-diagonal approximation with anisotropic thermal vibration parameters. The positional coordinates of the hydrogen atoms were refined together in one matrix starting from calculated positions. Their thermal vibration coefficients were

Table 2. *Anisotropic thermal vibration coefficients used in the formula*

$$\exp\{-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2hla^*c^*U_{13}+2klb^*c^*U_{23})\}$$

Estimated standard deviations are given in brackets.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0·056 (1)	0·040 (1)	0·042 (1)	0·001 (1)	0·011 (1)	0·011 (1)
C(2)	0·052 (1)	0·037 (1)	0·057 (2)	−0·010 (1)	0·013 (1)	−0·005 (1)
C(3)	0·035 (1)	0·048 (1)	0·050 (1)	−0·004 (1)	−0·007 (1)	−0·003 (1)
C(4)	0·054 (1)	0·039 (1)	0·037 (1)	0·001 (1)	−0·005 (1)	0·001 (1)
C(5)	0·045 (1)	0·036 (1)	0·036 (1)	−0·002 (1)	0·007 (1)	0·003 (1)
C(6)	0·030 (1)	0·048 (1)	0·039 (1)	−0·002 (1)	−0·001 (1)	0·004 (1)
C(7)	0·047 (1)	0·041 (1)	0·039 (1)	−0·011 (1)	−0·002 (1)	−0·004 (1)
C(8)	0·048 (1)	0·037 (1)	0·047 (1)	0·001 (1)	0·011 (1)	−0·009 (1)
C(9)	0·061 (1)	0·052 (1)	0·041 (1)	−0·001 (1)	0·018 (1)	−0·002 (1)
C(10)	0·047 (1)	0·051 (1)	0·047 (1)	0·012 (1)	0·003 (1)	0·013 (1)
C(11)	0·039 (1)	0·046 (1)	0·067 (2)	0·007 (1)	0·001 (1)	−0·002 (1)
O(12)	0·086 (1)	0·101 (2)	0·038 (1)	−0·000 (1)	−0·014 (1)	0·003 (1)
O(13)	0·061 (1)	0·088 (1)	0·053 (1)	−0·008 (1)	0·025 (1)	−0·008 (1)

Table 3. *C–H bond distances and related bond angles*

C–H (Å) (Mean e.s.d. 0·02 Å)		C–C–H (°) (Mean e.s.d. 1·2°)		H–C–H and related C–C–C (°) (Mean e.s.d. in H–C–H 1·7°)	
C(2)–H$_{\rm I}$	1·06	C(1)–C(2)–H$_{\rm I}$	112·2	H$_{\rm I}$—C(2)–H$_{\rm II}$	106·1
C(2)–H$_{\rm II}$	1·03	C(1)–C(2)–H$_{\rm II}$	109·1		
		C(3)–C(2)–H$_{\rm I}$	109·6	C(1)–C(2)–C(3)	114·7
		C(3)–C(2)–H$_{\rm II}$	104·7		
C(7)–H$_{\rm I}$	1·01	C(8)–C(7)–H$_{\rm I}$	109·0	H$_{\rm I}$—C(7)–H$_{\rm II}$	106·8
C(7)–H$_{\rm II}$	1·01	C(8)–C(7)–H$_{\rm II}$	111·2		
		C(6)–C(7)–H$_{\rm I}$	106·6	C(8)–C(7)–C(6)	114·1
		C(6)–C(7)–H$_{\rm II}$	108·8		
C(9)–H$_{\rm I}$	1·08	C(1)–C(9)–H$_{\rm I}$	107·0	H$_{\rm I}$—C(9)–H$_{\rm II}$	108·5
C(9)–H$_{\rm II}$	1·04	C(1)–C(9)–H$_{\rm II}$	109·7		
		C(8)–C(9)–H$_{\rm I}$	109·9	C(1)–C(9)–C(8)	108·9
		C(8)–C(9)–H$_{\rm II}$	112·8		
C(10)–H$_{\rm I}$	1·06	C(1)–C(10)–H$_{\rm I}$	109·0	H$_{\rm I}$—C(10)–H$_{\rm II}$	106·7
C(10)–H$_{\rm II}$	1·01	C(1)–C(10)–H$_{\rm II}$	105·8		
		C(6)–C(10)–H$_{\rm I}$	111·7	C(1)–C(10)–C(6)	113·7
		C(6)–C(10)–H$_{\rm II}$	109·6		
C(11)–H$_{\rm I}$	1·01	C(8)–C(11)–H$_{\rm I}$	105·6	H$_{\rm I}$—C(11)–H$_{\rm II}$	111·8
C(11)–H$_{\rm II}$	1·07	C(8)–C(11)–H$_{\rm II}$	108·8		
		C(3)–C(11)–H$_{\rm I}$	107·3	C(8)–C(11)–C(3)	113·8
		C(3)–C(11)–H$_{\rm II}$	109·6		
C(1)–H	1·03	C(9)—C(1)–H	106·5		
		C(2)—C(1)–H	109·1		
		C(10)–C(1)–H	108·3		
C(3)–H	1·04	C(2)—C(3)–H	107·6		
		C(11)–C(3)–H	109·3		
		C(4)—C(3)–H	103·4		
C(6)–H	1·04	C(10)–C(6)–H	111·0		
		C(7)—C(6)–H	106·0		
		C(5)—C(6)–H	102·5		
C(8)–H	1·00	C(9)—C(8)–H	108·5		
		C(11)–C(8)–H	108·0		
		C(7)—C(8)–H	106·8		

Table 4. *Coordinates of the atoms* (Å) *with respect to the three axes of inertia of the molecule.*

The masses of all non-hydrogen atoms are taken as equal. The x axis approximates the hypothetical twofold axis.

	x	y	z		x	y	z
C(1)	−1·502	−0·162	1·243	C(8)	−1·535	0·178	−1·211
C(2)	−0·631	1·087	1·433	C(7)	−0·693	−1·082	−1·431
C(10)	−0·694	−1·444	1·093	C(11)	−0·689	1·439	−1·110
C(3)	0·156	1·520	0·180	C(6)	0·121	−1·511	−0·207
C(4)	1·448	0·768	0·021	C(5)	1·422	−0·776	−0·042
O(12)	2·521	1·308	−0·054	O(13)	2·479	−1·349	0·058
C(9)	−2·403	0·025	0·027				

kept identical with those of the carbon atoms to which they are bonded. The observed structure factors were corrected for extinction according to Gomes de Mesquita (1967), which had only a slight effect.

Results and accuracy

The final reliability indices are $R_w = \sum w||F_o|-k|F_c||/\sum w|F_o| = 3{\cdot}7\%$ and $\sum w\Delta^2 = \sum w(|F_o|-k|F_c|)^2 = 3132$, including all reflexions within the limiting sphere.

The final lists of atomic parameters with their e.s.d.'s, are given in Tables 1 and 2. These e.s.d.'s, were derived from the 9×9 matrices of the block-diagonal approximation in the case of carbon and oxygen atoms with $m-n=1032-[(13\times 9)+1]=914$. Those of the hydrogen atoms were obtained from the 43×43 matrix with $m-n=1032-[(14\times 3)+1=989$. Interatomic distances, bond angles and dihedral angles for C and O atoms are given in Fig. 1. Table 3 contains C–H bond lengths and related bond angles. The list of observed and calculated structure factors may be obtained from the authors on request.

Molecular geometry

The shortness of the C=O bonds and the dihedral angle of only 11·9° suggest some type of conjugation in the dicarbonyl system, in agreement with the absorption spectrum ($\lambda_{\max}=418$ nm). The small values of the bond angles C(5)–C(4)–O(12) and C(4)–C(5)–O(13) and the short bond distances C(5)–C(6) and C(4)–C(3) combined with the long C(4)–C(5) bond are noteworthy. Many bond angles exceed the normal value in a tetrahedral configuration. This indicates considerable strain in the tricycloundecane system.

Table 5. *Shortest intermolecular distances*

C---C and C---O are below 3·75 Å, O---H and H---H are below 2·75 Å.

The following notation is used:

../1	Atom in molecule	$x'=x$	$y'=y$	$z'=z$
../2		$x'=\frac{1}{2}-x$	$y'=-y$	$z'=\frac{1}{2}+z$
../3		$x'=\frac{1}{2}+x$	$y'=\frac{1}{2}-y$	$z'=-z$
../4		$x'=-x$	$y'=\frac{1}{2}+y$	$z'=\frac{1}{2}-z$
$\pm a$		$x'\pm 1$	y'	z'
$\pm b$		x'	$y'\pm 1$	z'
$\pm c$		x'	y'	$z'\pm 1$

C(2)—O(12)/2+*b*−*c*	3·68 Å	H(1)—H(8)/1+*b*	2·59 Å
C(2)—O(13)/4+*c*	3·46	H(1)—H(3)/2+*b*−*c*	2·50
C(3)—O(12)/2−*c*	3·66	H(2)—O(13)/4+*c*	2·49
C(4)—O(13)/4−*b*+*c*	3·45	H(2)—H(11)/1+*b*	2·44
C(4)—O(13)/4+*c*	3·35	H(2)—H(7)/1+*b*	2·63
C(5)—C(5)/4−*b*+*c*	3·73	H(2)—H(6)/3+*c*	2·43
C(5)—C(5)/4+*c*	3·73	H(3)—H(1)/2+*b*	2·50
C(5)—O(12)/4−*b*+*c*	3·70	H(3)—H(8)/2	2·66
C(5)—O(13)/4−*b*+*c*	3·37	H(6)—H(2)/3−*a*+*c*	2·43
C(5)—O(13)/4+*c*	3·53	H(6)—H(11)/3−*a*+*c*	2·38
C(6)—O(12)/4−*b*+*c*	3·71	H(7)—O(13)/4−*b*+*c*	2·58
C(7)—O(12)/4−*b*+*c*	3·63	H(7)—H(2)/1−*b*	2·63
C(7)—O(13)/4−*b*+*c*	3·50	H(7)—H(10)/1−*b*	2·52
C(11)-O(12)/2−*c*	3·60	H(7)—H(9)/4−*b*	2·54
O(12)-C(2)/2+*b*	3·68	H(7)—H(10)/4−*b*	2·42
O(12)-C(3)/2	3·66	H(8)—H(3)/2−*c*	2·66
O(12)-C(5)/4+*c*	3·70	H(8)—H(1)/1−*b*	2·59
O(12)-C(6)/4+*c*	3·71	H(9)—H(7)/4	2·54
O(12)-C(7)/4+*c*	3·63	H(9)—H(10)/4−*b*	2·61
O(12)-C(11)/2	3·60	H(9)—H(11)/2−*c*	2·64
O(12)-O(13)/4+*c*	3·49	H(10)-H(7)/1+*b*	2·52
O(12)-O(13)/4−*b*+*c*	3·51	H(10)-H(7)/4	2·42
O(13)-C(4)/4+*c*	3·45	H(10)-H(9)/4	2·61
O(13)-C(4)/4−*b*+*c*	3·35	H(11)-H(2)/1−*b*	2·44
O(13)-C(5)/4+*c*	3·37	H(11)-H(6)/3+*c*	2·38
O(13)-C(5)/4−*b*+*c*	3·53	H(11)-H(9)/2	2·64
O(13)-O(12)/4+*c*	3·51		
O(13)-O(12)/4−*b*+*c*	3·49		
O(13)-O(13)/4−*b*+*c*	3·58		
O(13)-O(13)/4+*c*	3·58		
O(13)-H(2)/4−*b*+*c*	2·49		
O(13)-H(7)/4+*c*	2·58		

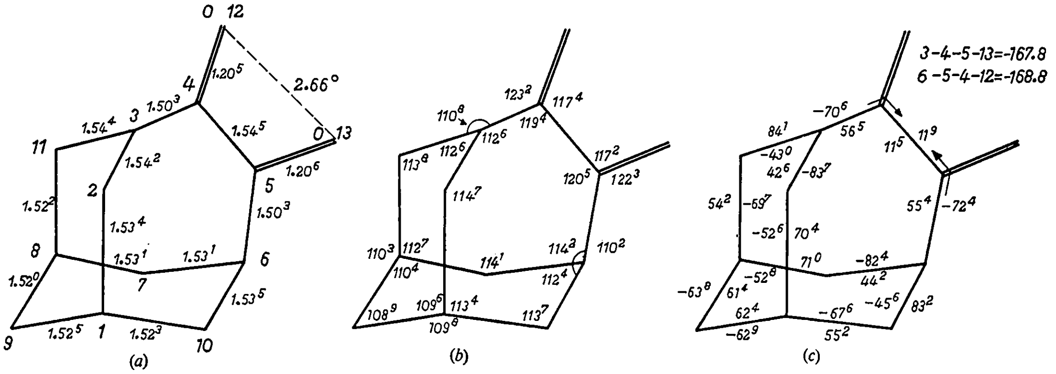

Fig. 1. (*a*) Interatomic distances in Å (mean e.s.d. 0·003 Å). (*b*) Bond angles (mean e.s.d. 0·2°). (*c*) Dihedral angles (mean e.s.d. 0·2°).

If the molecule had a twofold axis of symmetry it would coincide with one of its axes of inertia. We have determined these axes by the method as described by Rollett (1965). The coordinates of the atoms, in Å, with respect to these axes are given in Table 4. They show clearly that relatively large deviations from the twofold symmetry exist, most probably due to packing effects. The final difference Fourier synthesis did not show any significant features, leaving no room for another explanation.

The only striking feature with regard to the C–H angles is the low value of the angles C(4)–C(3)–H(3) and C(5)–C(6)–H(6) which may indicate an attraction of these hydrogen atoms by the oxygen atom O(12) and O(13) at O---H distances of 2·41 and 2·38 Å respectively.

Packing

Short intermolecular distances are presented in Table 5, from which it is concluded that each molecule is in contact with 12 others.

The arrangement of the molecules in the unit cell is shown in Fig. 2. The approximate plane of the dicarbonyl groups is almost normal to the *b* axis. These groups are close to the twofold screw axes at $(0,y,\frac{3}{4})$ and $(\frac{1}{2},y,\frac{1}{4})$ and thus form chains with strong dipole–dipole interactions. In these interactions the two carbonyl groups are not equivalent, which might cause the lack of symmetry in the molecule.

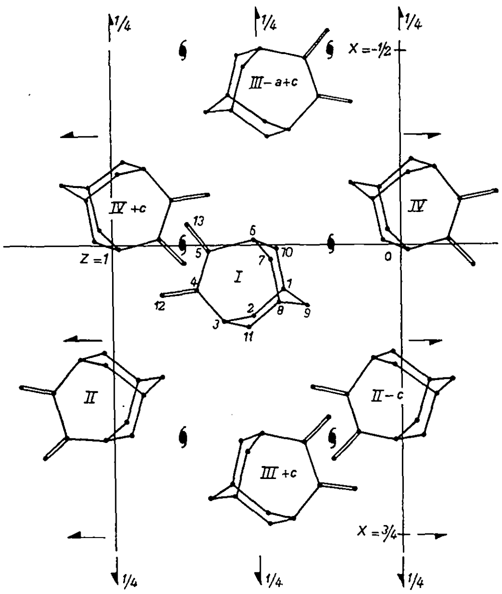

Fig. 2. Projection of the structure along the *b* axis. The molecules are marked as follows. (See also caption Table 5):

I = molecules at positions 1, $1+b$, $1-b$
II = molecules at positions 2, $2+b$
$\mathrm{II}-c$ = molecules at positions $2-c$, $2+b-c$
$\mathrm{III}+c$ = molecule at position $3+c$
$\mathrm{III}-a+c$ = molecule at position $3-a+c$
IV = molecules at positions 4, $4-b$
$\mathrm{IV}+c$ = molecules at positions $4+c$, $4-b+c$

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