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The Structure of Bicyclo[2,2,2]octene-2,3-*endo*-dicarboxylic Anhydride

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The crystal and molecular structure of bicyclo[2,2,2]-octene-2,3-*endo*-dicarboxylic anhydride, $C_{10}H_{10}O_3$, has been determined by direct methods and refined by least-squares. The crystals are monoclinic, space group $P2_1/c$, with $a=6{\cdot}534$, $b=10{\cdot}480$, $c=12{\cdot}184$ Å, $\beta=96{\cdot}37°$ and four molecules per unit cell. Intensity data for 1263 reflexions were collected on a PAILRED diffractometer from a crystal mounted along the *a* axis. The final *R* index for 967 reflexions with $I_0\geq 2\sigma(I_0)$ is 0·050; the average standard deviation in the atomic positions is about 0·003 Å for C and O and about 0·03 Å for H atoms. Within experimental error the molecule has symmetry *m*; there is no twisting from the 'eclipsed' conformation around the C(1)–C(4) axis. The anhydride group is significantly non-planar. The anisotropic temperature factors of the heavier atoms in the bicyclo-octene nucleus can be accounted for by a Schomaker–Trueblood rigid-body treatment; on this basis, corrections to the observed bond distances are in the range 0·008 to 0·012 Å. The thermal vibrations of the atoms in the anhydride group do not seem to correspond to the rigid-body motion of the rest of the molecule.

Introduction

Following our interest in the conformation of 'rigid' molecules with internal strain (Destro, Gramaccioli & Simonetta, 1968; Destro, Filippini, Gramaccioli & Simonetta, 1968; Bellobono, Destro, Gramaccioli & Simonetta, 1969; Destro, Filippini, Gramaccioli & Simonetta, 1969*a*, *b*, *c*), and in view of theoretical work on an extensive series of these compounds that we plan to carry out, it seemed to us particularly profitable to collect further accurate structural data on some bridged alicyclic anhydrides. Another point of interest for this particular compound is the absence of any accurate experimental data about the conformation of the bicyclo[2,2,2]oct-5-ene nucleus.

Experimental

Crystals of bicyclo[2,2,2]oct-5-ene-2,3-*endo*-dicarboxylic anhydride were obtained from the reaction of cyclohexa-1,3-diene with maleic anhydride and were recrystallized from a benzene–light petroleum solution.* They are prismatic, elongated along **a**. Weissenberg photographs indicated them to be monoclinic, with space group $P2_1/c$ (the systematic absences are 0*k*0 and *h*0*l* with *k* or *l* odd).

The unit-cell dimensions (see Table 1) were obtained from a least-squares fit to measurements of $\sin^2\theta$ for 37 0*kl* and 17 *hll* reflexions on zero-level Weissenberg photographs taken at 21 °C using Cu *Kα* radiation; the film was held in the asymmetric position, essentially following the Straumanis technique. Eccentricity coefficients were included as parameter in the least-squares calculations and weights were assigned as inversely proportional to $\sin^2 2\theta$.

Table 1. *Crystal data*

$C_{10}H_{10}O_3$		Mol. wt. 178·16
Monoclinic		Space group $P2_1/c$
$a=6{\cdot}534\pm0{\cdot}004$ Å		$\lambda(\text{Cu } K\alpha_1)=1{\cdot}54051$ Å
$b=10{\cdot}480\pm0{\cdot}001$		$\lambda(\text{Cu } K\alpha_2)=1{\cdot}54433$
$c=12{\cdot}184\pm0{\cdot}001$		$\lambda(\text{Cu } K\alpha)=1{\cdot}5418$
$\beta=96{\cdot}37°\pm0{\cdot}02°$		$\mu=8{\cdot}88$ cm^{-1}
$D_m=1{\cdot}43$ g. cm^{-3}		$D_x=1{\cdot}427$ g.cm^{-3}
$F(000)=376$	$Z=4$	$V=829{\cdot}24$ Å^3

The density was measured by flotation in a dilute Thoulet (K_2HgI_4) solution.

For determination of the structure, intensity data were collected on a Philips linear equi-inclination diffractometer (PAILRED) in the automatic mode using the ω-scan technique. Mo *Kα* radiation (monochromatized by a Si (111) single crystal) and a scintillation detector with pulse height analyser were used. The scan range varied from ±0·4° to ±1·3° (the larger values being used in the higher layers for low values of the *Υ* angle). The scan speed was 1°.min^{-1}; background counts were taken for 40 seconds at both ends of the scan, with crystal and counter stationary. Scanning was automatically repeated for each reflexion (up to a maximum of four times) until the number of scan counts reached at least the value of 1000. The layers 0 to 6 about the *a* axis were obtained from a crystal whose diameter was about 0·3 mm. A total of 1263 reflexions were measured and corrected for Lorentz and polarization factors. No corrections either for absorption or for secondary extinction were applied at this stage.

Solution and refinement of the structure

Approximate absolute scale and overall temperature factor were obtained by Wilson's method. For the solution of the phase problem by direct methods, the

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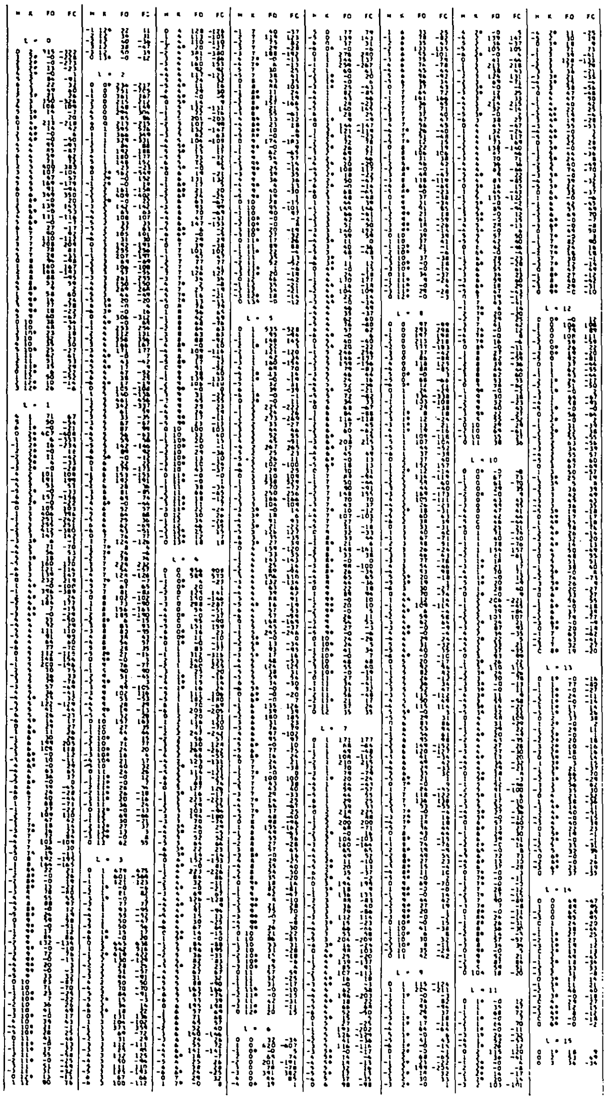
* We wish to thank Professor I. R. Bellobono for having kindly supplied us with the crystallized substance.

Table 2. *Observed and calculated structure factors*

The values have been multiplied by 10. Form factors for C and O atoms are taken from Cromer & Waber (1965) and for H atoms from Stewart, Davidson & Simpson (1965).



structure factors were converted to the normalized structure factors $|E_{hkl}|$ (Hauptman & Karle, 1953). The values of the statistical averages $\langle|E|\rangle$ and $\langle|E^2-1|\rangle$ are 0·829 and 0·916, respectively, in fair agreement with the values expected for a centrosymmetric structure. The sign determination was undertaken by applying the Sayre relationships (Sayre, 1952) to 162 reflexions with $|E|>1{\cdot}5$. The whole process was performed using a FORTRAN IV computer program (Long, 1965).

The E map (Karle, Hauptman, Karle & Wing, 1958), computed with the phases corresponding to the highest consistency index (0·84) revealed all the carbon and oxygen atoms. The structure-factor calculation including all the three-dimensional data gave an index $R=0{\cdot}28$.

Refinement was performed by a block-diagonal least-squares process, minimizing the function $\sum w(|F|_{\text{obs}}-|F|_{\text{calc}})^2$, using a program written by Albano, Domenicano & Vaciago (1966). During the first eight cycles ('shift factor' = 0·6) weights of the form $w=1/f^2$ were used, where f is the average scattering factor for all the atoms at the calculated value of $\sin\theta/\lambda$. The R factor reduced to 0·17. Weights were then changed to $w=1/\sigma^2(F)$, where $\sigma(F)$ was taken as $\sigma(F^2)/2F$ and computed from $\sigma^2F_o^2=\sigma_{\text{cs}}^2F_o^2+(AF_o^2)^2$. Here, $\sigma_{\text{cs}}^2(F_o^2)$ is the counting statistical variance and A an empirical parameter, which was chosen so as to make $w(\Delta F)^2$, the weighted mean quadratic error, approximately constant (within 10%) over the entire range of $|F_0|$'s (Peterson &Levy, 1957; Cruickshank & Pilling, 1961; Albano, Bellon, Chini & Scatturin, 1969). In the first cycles, A was taken equal to 0·02; it was changed during the course of the refinement to a final value of 0·08.

The R factor dropped (in two cycles) to 0·12 and, after a three-dimensional difference Fourier synthesis which indicated the positions of the hydrogen atoms, to 0·077 (in six cycles). During this stage, anisotropic temperature factors were assigned to carbon and oxygen atoms; the hydrogen atoms were only included in structure-factor calculations. At the end of this procedure, the 'goodness of fit' $[\sum w\Delta^2/(n-p)]^{1/2}$ was 1·61, significantly larger than the expected value of 1·0.

Table 3. *The heavy atom parameters and their standard deviations*

All the values in this table have been multiplied by 10^4. The temperature factor is in the form
$T_i=\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+2b_{12}hk+2b_{13}hl+2b_{23}kl)]$

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	759 (5)	8006 (3)	767 (3)	192 (10)	67 (3)	61 (2)	33 (4)	3 (3)	3 (2)
C(2)	1694 (5)	7400 (3)	1873 (2)	183 (8)	69 (3)	43 (2)	−5 (4)	12 (3)	−11 (2)
C(3)	3667 (5)	6694 (3)	1697 (2)	160 (8)	72 (3)	42 (2)	−2 (4)	−7 (3)	−4 (2)
C(4)	4084 (5)	6807 (3)	477 (2)	180 (9)	75 (3)	53 (2)	21 (4)	27 (3)	6 (2)
C(5)	2191 (6)	6348 (3)	−230 (3)	303 (12)	64 (3)	40 (2)	4 (4)	6 (3)	−4 (2)
C(6)	497 (6)	6965 (3)	−85 (2)	249 (11)	78 (3)	45 (2)	−17 (5)	−16 (4)	6 (2)
C(7)	2359 (6)	8955 (3)	426 (3)	290 (11)	59 (3)	75 (3)	5 (5)	18 (4)	5 (2)
C(8)	4350 (6)	8245 (3)	259 (4)	243 (11)	91 (4)	69 (3)	−26 (5)	32 (4)	13 (3)
C(9)	326 (6)	6397 (3)	2264 (3)	202 (11)	104 (4)	48 (2)	−23 (4)	10 (3)	−4 (2)
C(10)	3270 (5)	5337 (3)	2003 (2)	228 (10)	87 (4)	48 (2)	10 (5)	−1 (3)	12 (2)
O(1)	1336 (4)	5235 (2)	2361 (2)	256 (8)	88 (2)	68 (2)	−16 (3)	24 (3)	17 (1)
O(2)	−1391 (5)	6465 (3)	2483 (3)	214 (9)	165 (4)	111 (3)	−6 (4)	54 (3)	14 (2)
O(3)	4309 (5)	4417 (3)	1964 (2)	363 (9)	92 (3)	110 (2)	61 (4)	29 (3)	31 (2)

Further refinement was based on only those reflexions – 967 in number – whose intensity I_0 was greater than or equal to twice the standard deviation $\sigma(I_0)$. For these reflexions, the R index was 0·059 and the goodness of fit was 1·83; the formal standard deviations in the coordinates were approximately 10% larger than those calculated from the entire data set.

Full-matrix least-squares refinement was carried out, introducing as further variables the coordinates and isotropic temperature factors of the hydrogen atoms and a secondary extinction coefficient (Zachariasen, 1963). A modified version of the *ORFLS* program was used (Busing, Martin & Levy, 1962). After three cycles, no change in atomic parameters exceeded one third of its standard deviation. The R factor for the 967 reflexions dropped to 0·050 and the goodness of fit to 1·27; the bond distances and angles involving the hydrogen atoms were significantly improved. The final value for the secondary extinction parameter, Q (Larson, 1967, equation 3), was $12(\pm 3)\times 10^{-6}$.

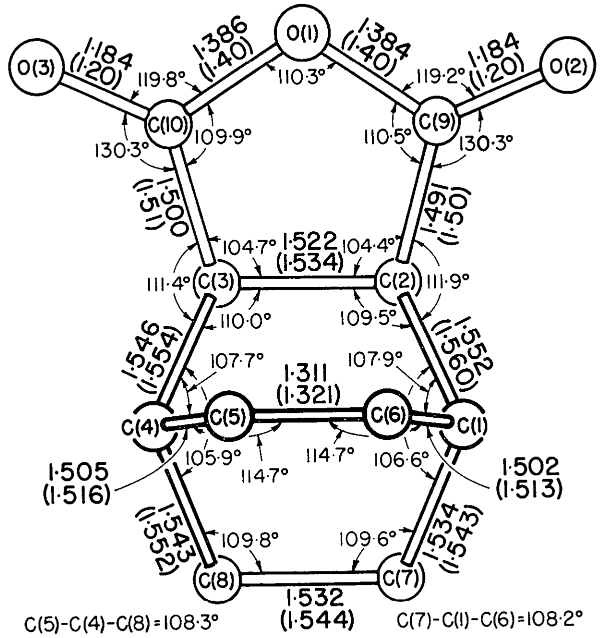


Fig. 1. The molecule of bicyclo[2,2,2]oct-5-ene-2,3-*endo*-dicarboxylic anhydride, seen along the direction corresponding to the maximum moment of inertia. The σ's in the bond distances are about 0·005 Å and in the angles about 0·3°. Values in parentheses include corrections for thermal motion.

Precision of the results

The observed and final calculated structure factors are listed in Table 2; the final parameters of the heavier atoms are given in Table 3 and of the hydrogen atoms in Table 4.

Table 4. *Parameters for the hydrogen atoms*

Values of x, y and z are multiplied by 10^3 and of B by 10

	x	y	z	B(Å^2)
H(1)	−52 (5)	844 (3)	89 (2)	44 (6)
H(2)	196 (6)	804 (3)	242 (3)	43 (7)
H(3)	484 (6)	701 (3)	218 (3)	32 (7)
H(4)	526 (6)	631 (3)	34 (3)	39 (7)
H(5)	236 (5)	565 (3)	−77 (2)	47 (6)
H(6)	−79 (5)	678 (3)	−52 (3)	48 (7)
H(7)	245 (5)	956 (3)	102 (3)	59 (7)
H(8)	167 (5)	941 (3)	−29 (3)	54 (6)
H(9)	553 (5)	854 (3)	74 (3)	57 (6)
H(10)	462 (7)	840 (4)	−47 (4)	68 (9)

The standard deviations in the coordinates of the heavier atoms, derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle, correspond to positional uncertainties of the order of 0·003 Å for the carbon and oxygen atoms and of 0·03 Å for the hydrogen atoms. The corresponding standard deviations in the bond distances involving only heavier atoms are around 0·005 Å and in the angles around 0·3°; in the C–H bonds they are around 0·04 Å and in the H–C–C and H–C–H angles 2 and 3°, respectively. A comparison between 'chemical equivalent' bond distances and angles seems to indicate that the reported precision is not overestimated.

Corrections for thermal libration

A 'rigid' molecule such as this anhydride was expected to behave as a rigid body in undergoing thermal libration. Accordingly, the tensors **T**, **L**, **S** (Schomaker & Trueblood, 1968), were derived from a least-squares treatment, using a FORTRAN IV program written by one of us (GF). In these calculations, equal weights were assigned to all thermal factors. The agreement

Table 5. *Rigid-body tensors for bicyclo*[2,2,2]*octene*-2,3-*endo-dicarboxylic anhydride*

The tensors are referred to a Cartesian coordinate system defined by unit vectors $\hat{\mathbf{a}}^*$, $\hat{\mathbf{b}}$, $\hat{\mathbf{a}}\times\hat{\mathbf{b}}^*$. All values have been multiplied by 10^4.

T(Å^2)	5551 (430)	−881 (91)	−356 (271)	
		500 (19)	−249 (70)	('unreduced')
			2700 (386)	
L(rad^2)	41 (6)	13 (4)	−1 (4)	
		65 (7)	−24 (5)	
			83 (7)	
S(Å. rad)	−10 (34)	43 (9)	−262 (48)	
	−278 (39)	41 (9)	−13 (34)	
	648 (54)	−114 (11)	−31 (35)	

between observed and calculated values of B_{ij}'s was good with the exception of B_{33} for C(9) and C(10), where the observed values were smaller than the calculated values, and O(1) and O(2), where the observed values were larger, the differences amounted to between three and five standard deviations. This is considered as evidence for significantly non-rigid behaviour of this portion of the molecule. Calculations were then repeated for the bicyclo-octene nucleus alone, excluding the anhydride group; the results are shown in Table 5. The agreement between observed and calculated values of B_{ij}'s was markedly improved, the differences now rarely exceeding the standard deviation, with a maximum of 2σ. The mean square rotational displacements of the bicyclo-octene nucleus amount to 33, 18, and 11(°)^2 about the principal axes of the tensor **L**.

Bond distances and angles involving the C and O atoms are shown in Fig. 1; values in parentheses include corrections for thermal motion. For the atoms of the bicyclo-octene nucleus, these corrections were derived from the formula proposed by Schomaker & Trueblood (1968), using the rigid-body parameters of Table 5. In view of the non-rigid-body motion of the atoms of the anhydride grouping, corrections to the bond distances involving these atoms have been estimated. Corrections to the bond angles are small (less than 0·1°), and have been neglected.

Distances and angles involving the hydrogen atoms are given in Table 6.

Table 6. *Bond distances and angles involving the hydrogen atoms*

C(1)–H(1)	0·98 Å	C(6)–H(6)	0·96 Å
C(2)–H(2)	0·95	C(7)–H(7)	0·96
C(3)–H(3)	0·97	C(7)–H(8)	1·05
C(4)–H(4)	0·96	C(8)–H(9)	0·97
C(5)–H(5)	1·00	C(8)–H(10)	0·94
C(2)—C(1)-H(1)	109°	C(6)–C(1)-H(1)	114°
C(7)—C(1)-H(1)	111	C(1)–C(2)-H(2)	110
C(3)—C(2)-H(2)	111	C(9)–C(2)-H(2)	110
C(2)—C(3)-H(3)	112	C(4)–C(3)-H(3)	110
C(10)–C(3)-H(3)	109	C(3)–C(4)-H(4)	111
C(5)—C(4)-H(4)	111	C(8)–C(4)-H(4)	113
C(6)—C(5)-H(5)	127	C(4)–C(5)-H(5)	118
C(5)—C(6)-H(6)	122	C(1)–C(6)-H(6)	123
C(1)—C(7)-H(7)	102	C(1)–C(7)-H(8)	106
C(8)—C(7)-H(7)	116	C(8)–C(7)-H(8)	113
H(7)—C(7)-H(8)	108	C(4)–C(8)-H(9)	108
C(4)—C(8)-H(10)	112	C(7)–C(8)-H(9)	113
C(7)—C(8)-H(10)	107	H(9)–C(8)-H(10)	107

Discussion

The molecule as viewed along the direction corresponding to the maximum moment of inertia is shown in Fig. 1. A stereoscopic illustration of the molecule, nearly along the same direction of Fig. 1, is shown in Fig. 2. The molecular symmetry is very close to *m*, no difference between the 'chemically equivalent' bond distance and angles exceeding 2σ. This strongly supports the point of view that the conformation here found is the same as in the isolated molecule, at least within the limits of our experimental results. A similar fact was observed also in 5-norbornene-2,3-*endo*-dicarboxylic anhydride (Destro, Filippini, Gramaccioli & Simonetta, 1969*c*).

Equations of the planes through the regions of the molecule which are of particular interest are given in Table 7, together with interplanar angles and the deviations of the individual atoms from the planes. Torsion angles are given in Table 8. Each of the four-membered rings (planes *A*, *B*, and *C*) is planar within the experimental uncertainty, and thus there is no significant twisting from the eclipsed conformations around the C(1)–C(4) axis. The eclipsed conformation also seems to be the stable one in bicyclo[2,2,2]octane (Ermer & Dunitz, 1969). The anhydride group (planes *D* and *D'*) is, however, far from planar, the bridging oxygen atom O(1) being displaced to one side of the mean plane and the terminal oxygen atoms O(2) and O(3) to the other side. The displacements are almost twice as large for the 5-norbornene derivative (Destro *et*

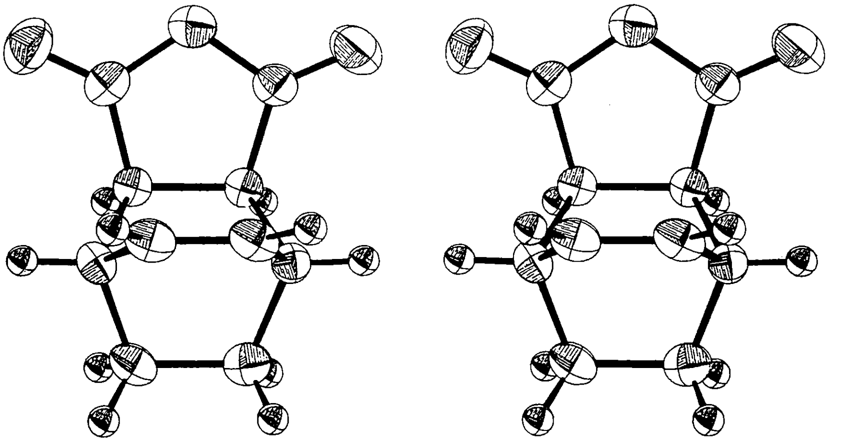


Fig. 2. A stereoscopic view of the molecule (Johnson, 1965).

al., 1969*a*, *b*, *c*), where a similar puckering was observed.

The bond distances and angles in the anhydride group are close to the corresponding ones in the 5-norbornene derivative (if data uncorrected for thermal libration are compared), and to the results obtained for succinic anhydride by Ehrenberg (1965) and by Biagini & Cannas (1965).

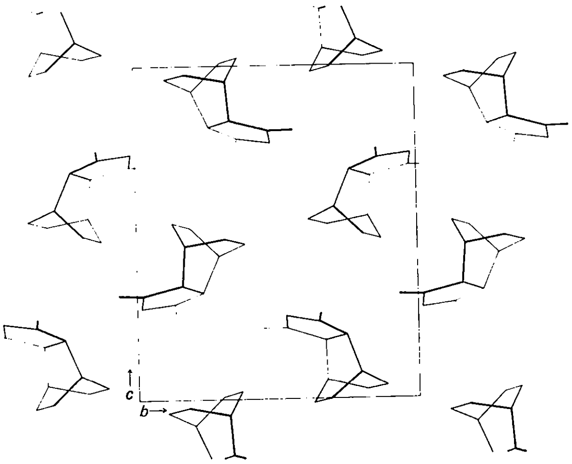


Fig. 3. Molecular packing seen along **a**.

Molecular packing

If we assume as van der Waals radii for carbon, oxygen, and hydrogen the values 1·8, 1·4, and 1·2 Å, respectively (Kitaigorodskii, 1961) we see that in only two cases do two atoms belonging to different molecules lie at a distance smaller than the sum of the corresponding van der Waals radii (see Table 9); even in these two cases the distance does not seem to be significantly smaller (within 3σ). Thus, there appears to be no strong intermolecular interaction, and a virtual absence of any molecular distortion connected with crystal packing. The molecular packing along **a** is shown in Fig. 3.

Table 9. *Intermolecular contact distances*

Uncorrected for thermal libration

C(5)-H(2)	$x,\ \frac{3}{2}-y,\ z-\frac{1}{2}$	2·92 Å
O(2)-H(3)	$x-1,\ y,\ z$	2·52

Table 7. *Some planes of interest*

The coefficients q_i are the direction cosines relative to the crystallographic axes **a**, **b** and **c**. In the least-squares treatment, the method described by Schomaker, Waser, Marsh & Bergman (1959) was adopted, with weights inversely proportional to the positional standard deviation along the normal to the plane. Atoms marked with an asterisk were omitted from least squares.

Plane *A*		Plane *B*		Plane *C*		Plane *D*		Plane *D'*	
	Δ		Δ		Δ		Δ		Δ
C(1)	0·001	C(1)	−0·001	C(1)	−0·001	C(2)	0·003	C(2)	0·006
C(2)	−0·001	C(4)	0·001	C(4)	0·001	C(3)	0·008	C(3)	0·006
C(3)	0·001	C(5)	−0·003	C(7)	−0·004	C(9)	−0·004	C(9)	−0·021
C(4)	−0·001	C(6)	0·003	C(8)	0·004	C(10)	0·004	C(10)	−0·019
						O(1)	0·045	O(1)	0·013
						O(2)	−0·046	*O(2)	−0·066
						O(3)	−0·044	*O(3)	−0·078

	q_1	q_2	q_3	D
Plane *A*	0·5073	0·8336	0·1607	−7·395 Å
Plane *B*	0·2601	0·6547	−0·7342	−4·937
Plane *C*	0·2318	0·1404	0·9309	−2·162
Plane *D*	0·2655	0·1921	0·9095	−3·857
Plane *D'*	0·2692	0·2057	0·9052	−3·954

Dihedral angle:	$A\wedge B$	121·5°	$A\wedge D$	120·9°
	$A\wedge C$	116·4	$A\wedge D'$	120·1
	$B\wedge C$	122·1		

Table 8. *Torsion angles*

The convention proposed by Klyne & Prelog (1960) is adopted.

C(1)—C(2)-C(3)—C(4)	−0·3°	C(2)-C(3)—C(4)—C(5)	−54·2°
C(3)—C(4)-C(5)—C(6)	57·8	C(4)-C(5)—C(6)—C(1)	−0·6
C(5)—C(6)-C(1)—C(2)	−57·1	C(6)-C(1)—C(2)—C(3)	54·6
C(6)—C(5)-C(4)—C(8)	−56·4	C(5)-C(4)—C(8)—C(7)	53·5
C(4)—C(8)-C(7)—C(1)	0·6	C(8)-C(7)—C(1)—C(6)	−54·8
C(7)—C(1)-C(6)—C(5)	57·9	C(7)-C(8)—C(4)—C(3)	−61·8
C(8)—C(4)-C(3)—C(2)	61·5	C(3)-C(2)—C(1)—C(7)	−61·4
C(2)—C(1)-C(7)—C(8)	61·0	C(9)-O(1)—C(10)-O(3)	−175·5
O(2)—C(9)-O(1)—C(10)	176·3	C(2)-C(9)—O(1)—C(10)	−3·6
C(9)—O(1)-C(10)-C(3)	3·5	O(1)-C(10)-C(3)—C(2)	−2·0
C(10)-C(3)-C(2)—C(9)	−0·0	C(3)-C(2)—C(9)—O(1)	2·1

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Verfeinerung der Kristallstruktur von ω-(p-Toluoyl)-acetophon-enol

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The crystal structure of *ω*-(*p*-toluoyl)-acetophenone enol ($C_{16}H_{14}O_2$) was refined by the least-squares method. This compound crystallizes in the space group *Pbca* with the lattice constants $a = 10{\cdot}428$, $b = 27{\cdot}427$ and $c = 8{\cdot}914$ Å; $Z = 8$. The *R* value was 0·050 based on the 1814 structure amplitudes used in the least-squares refinement, and 0·080 based on all the 2436 observed structure amplitudes. A hydrogen bond (O–H···O distance 2·458 Å) was found within the molecule. The structure is compared with that of the closely related compound, dibenzoylmethane.

Einführung

ω-(*p*-Toluoyl)-acetophenon-enol (TEN), $C_{16}H_{14}O_2$, wurde zusammen mit Dibenzoylmethan-enol (DBM) von Rösch (1927) kristalloptisch eingehend untersucht. Nach ihm kristallisieren die beiden Substanzen in Kristallklasse *mmm*, haben ähnliche Achsenverhältnisse und Habitus, und sehr hohe Doppelbrechung. Die Kristallstruktur des DBM wurde von Williams (1966) bestimmt und verfeinert. Zur Kristallstruktur des TEN wurden von Kato (1969) nur die Gitterkonstanten, die Raumgruppe und die groben Koordinaten von Kohlenstoff- und Sauerstoffatomen berichtet. Demnach ist das Bauprinzip der beiden Strukturen identisch. Um jedoch den Effekt der nur bei TEN vorhandenen Methylgruppe näher zu untersuchen, wurde die vorliegende Strukturverfeinerung vorgenommen.

Experimentelles

Das von Herrn Prof. Rösch freundlicherweise bereitgestellte Material wurde nach Umkristallisierung in Äthanol zur röntgenographischen Untersuchung herangezogen. Zur genauen Bestimmung der Gitterkonstanten wurden mit einer von Buerger (1937) beschriebenen Weissenberg-Kamera die nullten Schichten um die *a*- und *b*-Achse aufgenommen. Aus insgesamt 58 Cu $K\alpha_1$-, α_2- und α-Reflexen im Rückstrahlbereich er-