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The Structure of Bicyclo[2,2,1]hept-5-ene-2,3-*exo*-dicarboxylic Anhydride

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The crystal and molecular structure of bicyclo[2,2,1]hept-5-ene-2,3-*exo*-dicarboxylic anhydride has been determined and refined by least-squares methods. The crystals are orthorhombic, space group $P2_12_12_1$, with $a=7{\cdot}985$, $b=7{\cdot}630$, $c=12{\cdot}770$ Å and $Z=4$. Intensity data were collected visually from Weissenberg photographs. The solution of the phase problem was readily obtained by finding the orientation of a plausible molecular model with respect to the crystallographic axes as a result of a systematic search of the Patterson synthesis around the origin; the position of the molecule in the unit cell was then found by systematic structure-factor calculations. After refinement by least squares, the final R index was 0·086. The geometry of the bicyclo-heptene nucleus is in close agreement with the results found for the *endo* isomer: the bridge-head angle C(1)–C(7)–C(4) is 93·5°. Small but significant deviations from planarity are observed in the anhydride group.

Introduction

Since the extensive development of direct methods (Hauptman & Karle, 1953; Hauptman, 1964; Karle, 1964; Karle & Karle, 1966; Hauptman, Fischer, Hancock & Norton, 1969; Hauptman, 1970) solving light-atom structures with the help of the Patterson synthesis may seem a bit 'old-fashioned'. However, our feeling is that, at least in some cases, direct methods do not yet have an overwhelming advantage over other alternatives. For instance, the non-centrosymmetric structure of a crystal containing rigid molecules of roughly known conformation (a case which is indeed rather common) may be easily solved by means of the Patterson synthesis, and when the interpretation of the Patterson function is somewhat 'automated', solution may become a mere matter of a few minutes with a modern computer, in excellent comparison with direct methods.

As a first example we considered the structure of bicyclo[2,2,1]hept-5-ene-2,3-*exo*-dicarboxylic anhydride, a bridged alicyclic compound, the *endo* isomer of which had already been studied in this laboratory (Destro, Filippini, Gramaccioli & Simonetta, 1969), in line with a systematic study of a series of chemically related substances (Destro, Filippini, Gramaccioli & Simonetta, 1969, 1971; Filippini & Simonetta, 1970).

The knowledge of an accurate experimental conformation of these molecules was considered necessary in view of theoretical work we are carrying out on an extensive series of rigid molecules with internal strain.

Experimental

Crystals of bicyclo[2,2,1]hept-5-ene-2,3-*exo*-dicarboxylic anhydride were obtained by heating to 190°C the *endo* isomer obtained from the reaction of cyclopentadiene with maleic anhydride, and were recrystallized from benzene/light petroleum. They are bispheroidal, elongated along **c**.

Weissenberg photographs indicated the crystals to be orthorhombic, space group $P2_12_12_1$ (the systematic absences are $h00$, $0k0$, $00l$ with h, k or l odd).

The unit-cell dimensions (Table 1) were obtained from a least-squares fit to measurements of $\sin^2\theta$ for 23 $hk0$ and 29 hhl reflexions on zero-level Weissenberg photographs taken at 21 °C with Cu $K\alpha$ radiation, the film being held in the asymmetric position, essentially following the Straumanis technique. Eccentricity coefficients were included as parameters in the least-squares calculations and weights were assigned as inversely proportional to $\sin^2 2\theta$.

Table 1. *Crystal data for bicyclo*[2,2,1]*hept*-5-*ene*-2,3-*exo-dicarboxylic anhydride*

M.W. 164·16 $Z=4$
$D_m=1{\cdot}423$ $D_x=1{\cdot}401$ g.cm^{-3}
$F(000)=344$
$a=$ 7·9850 ± 0·0020 Å
$b=$ 7·6300 ± 0·0050
$c=$ 12·7700 ± 0·0020
$V=778{\cdot}0$ Å^3
$\lambda(\text{Cu }K\alpha_1)=1{\cdot}54051$ Å
$\lambda(\text{Cu }K\alpha_2)=1{\cdot}54433$
$\lambda(\text{Cu }K\alpha)=1{\cdot}5418$

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

For the determination and refinement of the structure, intensity data were collected from multiple-film equi-inclination Weissenberg photographs. The layers 0–10 along **c** and 0–7 along [1$\bar{1}$0] were obtained from two crystals, almost square in section, whose diameter was about 0·2 mm. Copper $K\alpha$ radiation was used. The intensities were estimated visually and corrected for Lorentz and polarization factors. No correction was made either for absorption or for extinction.

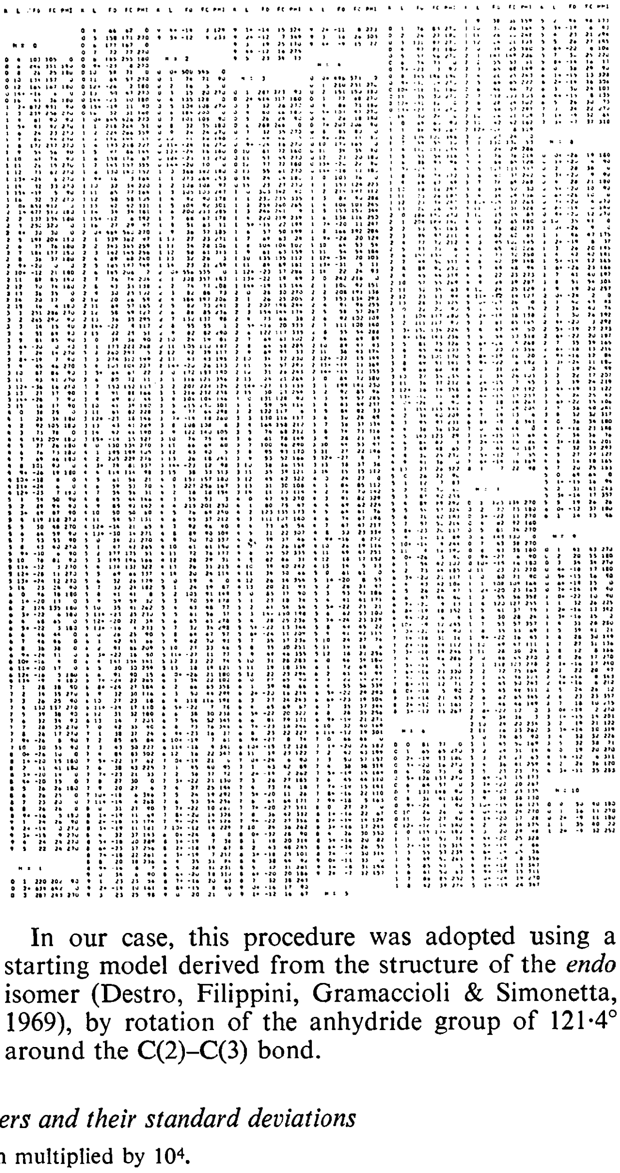
The processing of the observed data was first carried out within the single layers, obtaining film and scale factors by minimizing $\sum(\ln I_i - \ln KI_j)^2$ as indicated by Rae (1965). Standard deviations were assigned to single observations by means of an analysis of the residuals (Gramaccioli & Mariani, 1967). The evaluation of relative scale factors for all the layers and subsequent averaging of the observed F_0^2 values were performed according to the method proposed by Rollett and Sparks, modified to account for the dependence of weights upon the final scale factors (Hamilton, Rollett & Sparks, 1965; Duchamp, 1964). The final reduced set contains 988 reflexions out of 1053 within the effective Cu $K\alpha$ sphere, of which 284 were too weak to be observed ('less than').

Determination and refinement of the structure

It is well known that the orientation can be easily deduced for a rigid molecular group by a systematic search of the Patterson synthesis (Nordman & Nakatsu, 1963; Huber, 1965; Nordman, 1966; Hoppe & Paulus, 1967; Braun, Hornstra & Leenhouts, 1969). Programs written in this laboratory in the Fortran IV language for orthorhombic, monoclinic and triclinic crystals (Filippini & Gramaccioli, 1969; Bianchi, 1972) have been successfully applied to the solution of other structures (Gavezzotti, Mugnoli, Raimondi & Simonetta, 1972; Gramaccioli & Simonetta, 1971; Bianchi, Mugnoli & Simonetta, 1972). The method is essentially close to the procedure adopted by Nordman (1966): the sharpened Patterson function (not necessarily on an absolute scale or with manipulations at the origin), evaluated at intervals of about 0·1 Å along the three crystallographic axes, is considered for this purpose only within 3·2 Å from the origin (this excludes all intermolecular vectors) and stored in the memory of the computer. A map of the 'sum function' (Buerger, 1959) is calculated for intervals of 7·5° in the rotation angles of the model. The correct orientation corresponds to one of the highest peaks (usually the highest or next highest) and no serious trouble was encountered even in cases of some complexity; the computing time has never exceeded one minute for a computer such as UNIVAC 1108.

Table 2. *Observed and calculated structure factors*

All F values have been multiplied by 10. 'Less than' reflexions are indicated as negative F_o. Reflexions omitted from the final least-squares cycles are marked by an asterisk. Form factors for heavier atoms were taken from Cromer & Waber (1965) and for H atoms from Stewart, Davidson & Simpson (1965).



In our case, this procedure was adopted using a starting model derived from the structure of the *endo* isomer (Destro, Filippini, Gramaccioli & Simonetta, 1969), by rotation of the anhydride group of 121·4° around the C(2)–C(3) bond.

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

All the values have been multiplied by 10^4.

The temperature factor is in the form $\exp\left[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)\right]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	1776 (8)	3341 (7)	−2155 (5)	151 (9)	143 (9)	70 (4)	−24 (9)	−20 (5)	−14 (5)
C(2)	2821 (6)	5075 (8)	−2148 (4)	127 (8)	146 (9)	44 (3)	−3 (9)	2 (4)	6 (5)
C(3)	2585 (6)	5739 (7)	−1019 (4)	120 (7)	155 (9)	45 (3)	2 (7)	−4 (4)	−16 (5)
C(4)	1487 (8)	4311 (10)	−507 (4)	163 (10)	266 (14)	35 (2)	−25 (11)	8 (5)	9 (6)
C(5)	−195 (8)	4481 (11)	−1052 (6)	128 (9)	246 (14)	89 (5)	−23 (10)	16 (6)	12 (7)
C(6)	−10 (8)	3929 (9)	−2015 (5)	147 (10)	213 (13)	82 (4)	−35 (10)	−14 (6)	2 (6)
C(7)	2155 (7)	2637 (8)	−1064 (5)	146 (10)	169 (11)	84 (4)	−28 (9)	−20 (5)	39 (6)
C(8)	4638 (7)	4727 (8)	−2250 (5)	133 (9)	156 (11)	87 (5)	3 (9)	24 (6)	7 (6)
C(9)	4331 (7)	5771 (8)	−584 (5)	148 (9)	161 (10)	74 (4)	−15 (10)	−32 (5)	−11 (6)
O(1)	5469 (5)	5127 (6)	−1320 (4)	110 (6)	241 (10)	105 (4)	6 (7)	−20 (4)	−2 (5)
O(2)	5434 (7)	4130 (8)	−2968 (4)	205 (9)	349 (13)	113 (4)	13 (10)	75 (5)	−23 (7)
O(3)	4801 (7)	6184 (7)	265 (4)	271 (11)	295 (11)	88 (4)	−51 (10)	−68 (5)	−41 (5)

The highest value of the sum function proved to correspond to the correct molecular orientation. Since at that time a 'translational' search program had not yet been written in our laboratory, when the orientation was known, the position of the molecule in the unit cell was found by carrying out a series of structure factor calculations on the *xz* and *yz* projections, each time assigning a different set of coordinates to the centre of the molecule and recording a map of discrepancy indices *R*.*

The *R* index of the 'best' result from these calculations was 0·23 for all the observed reflexions with $\sin^2\theta/\lambda^2 \le 0{\cdot}20$. Refinement of the position of the heavier atoms by block-diagonal least squares was then initiated,* minimizing the function $\sum w(|F_o|-|F_c|)^2$ and using weights of the form $w=1/f^2$, where f is the average scattering factor for all the atoms at the calculated value of $\sin\theta/\lambda$. All temperature factors were considered as isotropic. After three cycles, the *R* index was 0·17. The refinement was continued by full-matrix least squares, using the *ORFLS* program (Busing, Martin & Levy, 1962). Anisotropic temperature factors were adopted for carbon and oxygen atoms; the hydrogen atoms were included only in the structure factor calculations, with positional coordinates derived from the presumed molecular geometry, and isotropic temperature factors of 5 Å^2. Weights were assigned equal to $1/\sigma^2$, where σ^2 is the variance in F_o derived in our data reduction. After six cycles, the *R* index had dropped to 0·098.

At this stage, a check of our weighting scheme was considered necessary, by examining the distribution of $w(|F_o|-|F_c|)^2$ over the entire range of $|F_o|$. For this purpose, reflexions were divided into four groups, each containing an equal amount of data. Instead of being approximately constant (Cruickshank, 1961), a considerable variation of $w(|F|_o-|F|_c)^2$ was found, the values ranging in the ratio 1:2 and the 'goodness of fit', $[\sum w(|F_o|-|F_c|)^2/(n-p)]^{1/2}$, was 5·56. These two facts did not give us great confidence in our weights. Therefore, the final weights were assigned as $w=1/(a+b|F_o|+c|F_o|^2)$ (Cruickshank, 1961), where *a*, *b* and *c* were obtained from a least-squares fit of $(|F_o|-|F_c|)^2$ as a function of $|F_o|$. Owing to some irregularity in the distribution of $w\Delta F^2$ as a function of $|F_o|$, the ΔFs were fitted to two parabolae, one for $F_o \le 16$ and the other for $F_o > 16$.

After two further cycles of full-matrix least squares, the *R* index was 0·086. No parameter shifts exceeded 0·3 times the corresponding standard deviation.

Precision of the results

The observed and the final calculated structure factors are listed in Table 2; the final parameters of the heavier atoms are given in Table 3 and the 'geometrical' coordinates of the hydrogen atoms in Table 4. The standard deviations in the coordinates of the C and O 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 0·007 Å. The corresponding standard deviations in the bond distances are around 0·009 Å and in the bond angles around 0·5°.

Table 4. *Parameters for the hydrogen atoms*

	x	*y*	*z*	*B*(Å^2)
H(1)	0·200	0·253	−0·275	5·0
H(2)	0·239	0·591	−0·268	5·0
H(3)	0·203	0·692	−0·101	5·0
H(4)	0·148	0·427	0·028	5·0
H(5)	−0·127	0·495	−0·075	5·0
H(6)	−0·090	0·389	−0·256	5·0
H(7)	0·340	0·254	−0·098	5·0
H(8)	0·140	0·162	−0·092	5·0

Corrections for thermal libration

The molecule of bicyclo [2,2,1] hept-5-ene-2,3-*exo*-dicarboxylic anhydride is substantially rigid and is therefore expected to behave as a rigid body in undergoing thermal libration. Accordingly, the tensors **T**, **L** and **S** (Schomaker & Trueblood, 1968) were derived from a least-squares treatment, using a program written by one of us (G.F.). In these calculations, equal weights were assigned to all thermal factors; the results are shown in Table 5. The agreement between observed and calculated values of B_{ij} for each atom is fairly good, nearly all the differences being within 3 times the standard deviation. The temperature ellipsoids are shown in Fig. 1.

Table 5. *Rigid-body tensors for bicyclo* [2,2,1] *heptene-2,3-exo-dicarboxylic anhydride*

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

T (Å^2)	1298 (124)	−625 (70)	−123 (87)
		1264 (68)	956 (80)
			1952 (139)
L (rad^2)	99 (10)	7 (6)	21 (4)
		84 (5)	3 (5)
			47 (7)
S (Å . rad)	101 (20)	−257 (23)	−360 (33)
	151 (24)	−10 (16)	128 (23)
	171 (27)	−152 (17)	−91 (20)

The mean square rotational displacements of the molecule amount to 35, 27, 13 (°)^2 about the principal axes of the tensor **L**.

The correction to the distances was derived, under the rigid-body assumption, from the tensor **L**, according to Schomaker & Trueblood (1968). This procedure resulted in a substantial increase (around 0·013 Å) in all of them; a negligible correction for the bond angles (less than 0·1°) was found. Values for all bond distances before and after correction for thermal libration are given in Table 6, and torsion angles in Table 7.

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* For these purposes, programs written by Albano, Bellon, Pompa & Scatturin (1963 *a* and *b*) were used.

Table 6. *Bond distances and angles*

	Uncorrected	Corrected
C(1)–C(2)	1·565 Å	1·575 Å
C(1)–C(6)	1·505	1·516
C(1)–C(7)	1·523	1·536
C(3)–C(2)	1·540	1·554
C(2)–C(8)	1·481	1·491
C(3)–C(4)	1·544	1·555
C(3)–C(9)	1·501	1·510
C(4)–C(5)	1·519	1·528
C(4)–C(7)	1·556	1·569
C(5)–C(6)	1·308	1·320
C(8)–O(1)	1·394	1·405
C(8)–O(2)	1·204	1·216
C(9)–O(1)	1·396	1·409
C(9)–O(3)	1·190	1·199

C(2)–C(1)–C(6)	104·6°
C(2)–C(1)–C(7)	100·8
C(6)–C(1)–C(7)	100·6
C(1)–C(2)–C(3)	102·6
C(1)–C(2)–C(8)	111·8
C(3)–C(2)–C(8)	105·2
C(2)–C(3)–C(4)	103·5
C(2)–C(3)–C(9)	103·8
C(4)–C(3)–C(9)	112·5
C(3)–C(4)–C(5)	104·4
C(3)–C(4)–C(7)	101·0
C(5)–C(4)–C(7)	99·4
C(4)–C(5)–C(6)	107·6
C(5)–C(6)–C(1)	108·3
C(1)–C(7)–C(4)	93·5
C(2)–C(8)–O(1)	110·6
C(2)–C(8)–O(2)	130·7
O(1)–C(8)–O(2)	118·7
C(3)–C(9)–O(1)	110·5
C(3)–C(9)–O(3)	129·4
O(1)–C(9)–O(3)	120·1
C(8)–O(1)–C(9)	110·0

Discussion

The molecule as viewed along the direction corresponding to the maximum moment of inertia is shown in Fig. 1. The molecular symmetry is very close to *m*, no difference between the 'chemically equivalent' bond distances and angles exceeding 3σ. This strongly supports the view that the conformation found here is very close to that of the isolated molecule, at least within the limits of our experiment. A similar observation was also made for the *endo* isomer and for bicyclo[2,2,2]oct-5-ene-2,3-*endo*-dicarboxylic anhydride (Destro, Filippini, Gramaccioli & Simonetta, 1969, 1971).

The conformation of the bicyclo nucleus is in essential agreement with the results of previous crystallographic work, such as the structures of *anti*-7-norbornenyl-*p*-bromobenzoate (Macdonald & Trotter, 1965 *b*), of cyclopentadiene dimer (Bellobono, Destro, Gramaccioli & Simonetta, 1969) and of bicyclo[2,2,1]hept-5-ene-2,3-*endo*-dicarboxylic anhydride (Destro, Filippini, Gramaccioli & Simonetta, 1969).

The value of the 'bridge-head' angle C(1)–C(7)–C(4) is very far from the tetrahedral value, as in most of these compounds. Our result (93·5°), almost the same as in the *endo* isomer (93·4°), is close to the value 92·7° found in the cyclopentadiene dimer and to 93·2 and 92·0° obtained for norbornane and norbornadiene respectively, by electron diffraction in the gas phase (Morino, Kuchitsu & Yokozechi, 1967). Our result therefore fully confirms these values, the angles reported by Macdonald & Trotter (1965 *a*, *b*) being slightly larger (96 and 97 ± 1·2° in the tricyclooctane and the norbornene nuclei respectively). The difference between these two and the others is at the limit of significance: it may well be connected with the fact that in both compounds a *p*-bromobenzoyl group is attached to the 'apical' position of the bridge.

On the whole, the bond lengths and angles are very close to the corresponding ones in the *endo* isomer, the

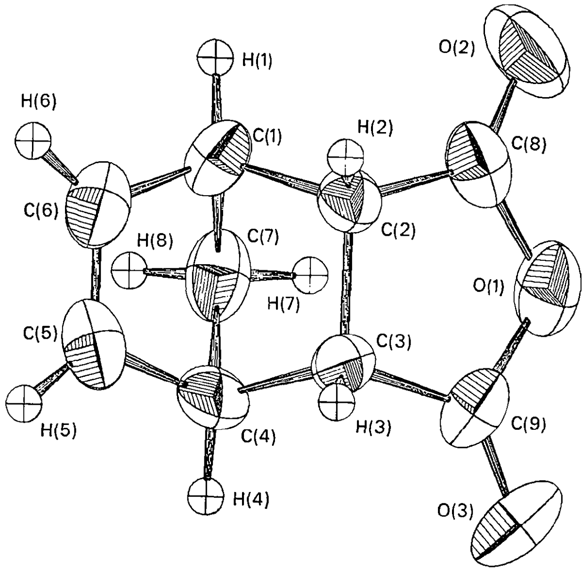

Fig. 1. The molecule of bicyclo[2,2,1]hept-5-ene-*exo*-dicarboxylic anhydride viewed along the direction corresponding to the maximum moment of inertia.

Table 7. *Torsion angles*

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

C(1)–C(6)–C(5)–C(4)	0·9°	C(6)–C(5)–C(4)–C(3)	70·3°
C(5)–C(4)–C(3)–C(2)	−68·2	C(4)–C(3)–C(2)–C(1)	1·4
C(3)–C(2)–C(1)–C(6)	66·1	C(2)–C(1)–C(6)–C(5)	−71·2
C(2)–C(1)–C(7)–C(4)	57·6	C(1)–C(7)–C(4)–C(3)	−56·8
C(7)–C(4)–C(3)–C(2)	34·6	C(3)–C(2)–C(1)–C(7)	−37·8
C(6)–C(5)–C(4)–C(7)	−33·6	C(5)–C(4)–C(7)–C(1)	49·8
C(4)–C(7)–C(1)–C(6)	−49·6	C(7)–C(1)–C(6)–C(5)	33·0
C(3)–C(9)–O(1)–C(8)	2·7	C(9)–O(1)–C(8)–C(2)	−1·3
O(1)–C(8)–C(2)–C(3)	−0·5	C(8)–C(2)–C(3)–C(9)	2·0
C(8)–C(2)–C(1)–C(6)	178·5	C(5)–C(4)–C(3)–C(9)	179·5
C(3)–C(2)–C(8)–O(2)	176·8	C(2)–C(3)–C(9)–O(3)	−179·7
O(3)–C(9)–O(1)–C(8)	179·8	C(9)–O(1)–C(8)–O(2)	−179·0
C(8)–C(2)–C(1)–C(7)	74·5	C(7)–C(4)–C(3)–C(9)	−76·7
C(1)–C(2)–C(3)–C(9)	119·0	C(4)–C(3)–C(2)–C(8)	115·6
C(1)–C(2)–C(8)–O(1)	111·1	C(4)–C(3)–C(9)–O(1)	108·4
C(1)–C(2)–C(8)–O(2)	66·2	C(4)–C(3)–C(9)–O(3)	−68·4

difference in most cases not being significant (within 3σ). Slight differences are found for some angles, such as C(2)–C(1)–C(7) and its chemical equivalent, which are both larger (100·8 and 101·0° respectively) than the corresponding angles in the *endo* isomer (97·8 and 97·7° respectively). The angle C(3)–C(4)–C(5) and its equivalent (104·4 and 104·6° respectively) are smaller than in the *endo* isomer (108·1 and 106·5° respectively).

The angles C(1)–C(2)–C(8) and their 'equivalent' are 111·8 and 112·5° respectively, in comparison with 113·6 and 114·6° for the *endo* isomer, the difference here being at the limit of significance. This fact is rather surprising because, at a rough evalution, these angles would be expected to differ by a larger amount, owing to the rotation of the anhydride group with respect to the bicycloheptene nucleus.

The geometry of the anhydride group is in close agreement with the results found for other anhydrides (Ehrenberg, 1965; Biagini & Cannas, 1965; Destro, Filippini, Gramaccioli & Simonetta, 1969, 1971). As in the *endo* isomer and in bicyclooctene-*endo*-dicarboxylic anhydride there are small, but significant, deviations from planarity; in our compound, however, they are still smaller, the largest of them being only 0·020 Å, in comparison with 0·035 Å for the *endo* isomer and 0·046 Å for the bicyclooctene derivative.

Equations of the planes through the regions of the molecule which are of particular interest are given in Table 8, together with interplanar angles and deviations of the individual atoms for the planes. These deviations in the anhydride group bear no relationship to the *endo* isomer.

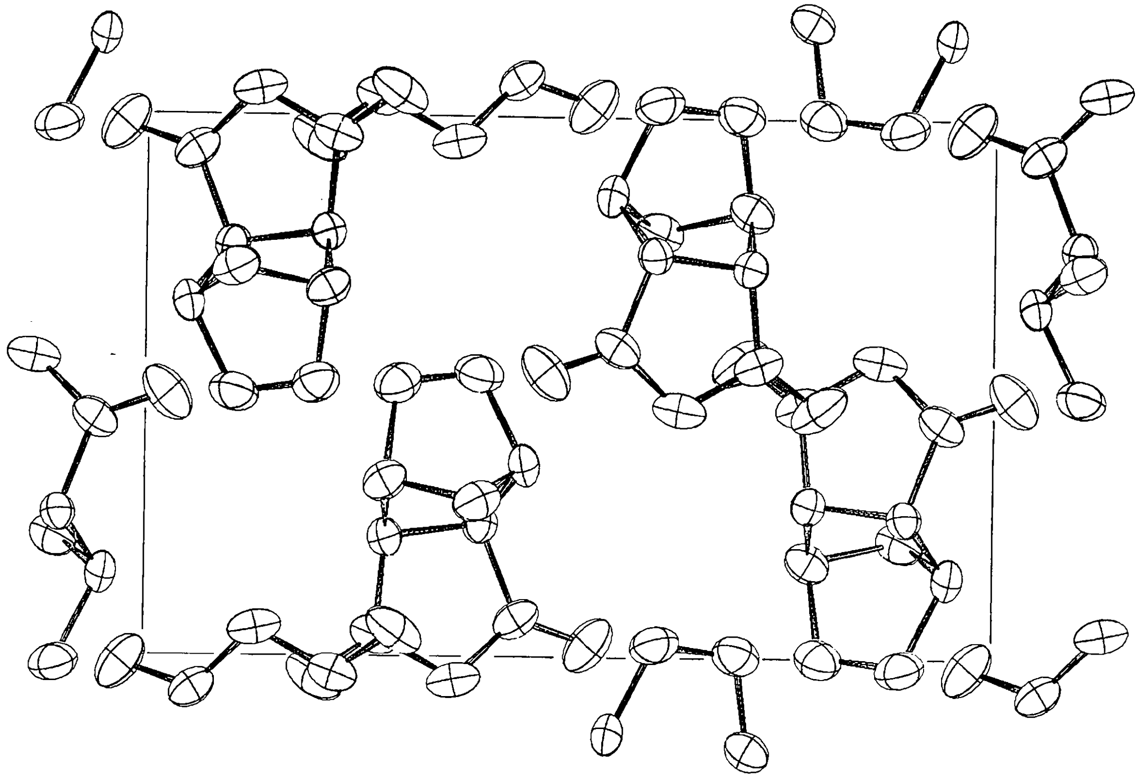

Fig. 2. Molecular packing as seen along **b**.

Table 8. *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 the least squares.

Plane *A*		Plane *B*		Plane *C*		Plane *D*		Plane *D'*	
C(1)	0·007	C(1)	−0·002	C(1)	0·000	C(2)	0·008	C(2)	0·015
C(2)	−0·008	C(4)	0·003	C(4)	0·000	C(3)	−0·013	C(3)	−0·020
C(3)	0·007	C(5)	−0·006	C(7)	0·000	C(8)	0·002	C(8)	0·015
C(4)	−0·008	C(6)	0·005			C(9)	0·021	C(9)	0·014
						O(1)	−0·009	O(1)	−0·003
						*O(2)	−0·039	O(2)	−0·015
						*O(3)	0·014	O(3)	0·000

Table 8 (*cont.*)

Plane	q_1	q_2	q_3	D
A	−0·8174	0·5061	−0·2751	−0·888 Å
B	0·2490	0·9227	−0·2943	−3·544
C	0·9134	0·4050	−0·0416	−2·460
D	0·1375	0·9357	−0·3249	−4·852
D'	0·1407	0·9326	−0·3325	−4·862

Dihedral angle				
	$A \wedge B$	110·2°	$A \wedge D$	116·8°
	$A \wedge C$	122·0	$A \wedge D'$	116·6
	$B \wedge C$	127·8		

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 (Kitaigorodsky, 1961), we see that only in two cases do two atoms belonging to different molecules lie at a distance smaller than the sum of the corresponding van der Waals radii. A summary of these distances is given in Table 9. The molecular packing seen along **b** is represented in Fig. 2.

Table 9. *Intermolecular contact distances* (*uncorrected for thermal libration*)

C(9)–O(2)	$1-x$,	$\frac{1}{2}+y$,	$-\frac{1}{2}-z$	3·17 Å
O(3)–H(6)	$\frac{1}{2}+x$,	$\frac{1}{2}-y$,	$-z$	2·48

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