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The Crystal and Molecular Structure of a Tetracyclic Bromobenzoate, $C_{21}H_{23}O_2Br$*

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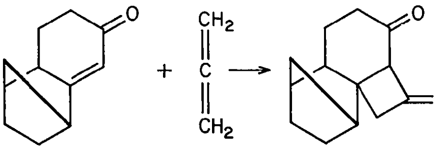
The title compound, $C_{21}H_{23}O_2Br$, is part of the skeleton of the aconite alkaloids. The crystals are in space group $P2_1/c$ with $a=6{\cdot}312$ (3), $b=15{\cdot}577$ (3), $c=18{\cdot}267$ (5) Å, $\beta=90{\cdot}99$ (3)°, $Z=4$. The structure was determined by the heavy-atom method, and refined by block-diagonal least-squares calculations to $R=0{\cdot}046$ for the 2545 observed reflexions. The strain caused by the fusion of rings in the molecule results in considerable variations in the C–C single-bond lengths to values between 1·500 and 1·587 (5) Å, the longest being that shared by the six- and four-membered rings.

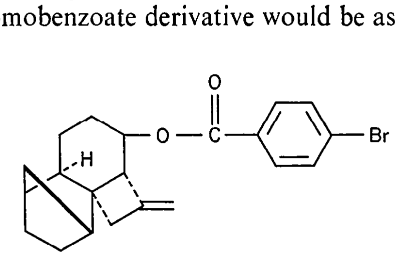
Introduction

In the course of the synthesis of aconite alkaloids developed by K. Wiesner and his collaborators it was essential to prepare a photochemical addition compound from an α,β unsaturated ketone and allene. Wiesner, Poon, Jirkovský & Fishman (1969) proposed that the stereochemistry of this photo-addition is controlled by the tendency of the excited state to exist preferentially in the most stable configuration. The excited state was assumed to have carbonium character in the α position to the carbonyl group and an orbital with an electron pair in the β position. This general rule was applied to a number of similar syntheses where the orbital and the adjacent hydrogen were *trans*. In order to test Wiesner's general rule in a completely different example, a tetracyclic compound (I), related to aconite alkaloids, was synthesized and its adduct (II) was obtained.



(I) (II)

Wiesner predicted that in (II) the orbital and the adjacent hydrogen are *cis* and that the stereochemistry of its bromobenzoate derivative would be as in (III).



(III)

The structure described here was found to consist of (III) and its enantiomer.

Experimental

Preliminary study of the crystals and space group was carried out with precession photographs. The colourless monoclinic prisms, crystallized from pentane, were elongated along **a** and had (011) faces prominently developed. The cell dimensions and intensities were measured on a G.E. XRD-5 manual diffractometer, with Cu radiation and a Ni filter. The crystal was cut into a sphere 0·33 mm in diameter and mounted along **a***. The cell parameters were calculated from the 2θ values of the strongest intermediate- and high-order axial reflexions, measured at a take-off angle of 1·0° and with narrow slits of 0·02 and 0·05°. The crystal data are presented in Table 1. The intensities were measured by the stationary-crystal stationary-counter method at 3·5° take-off angle with open counter window, counting for 10 s at the $K\alpha_1$ peak position and for another 10 s at the background on the lower side of the peak. The net integrated intensities were then estimated from these counts with a conversion table calibrated at varying values of 2θ to allow for the separation of the $K\alpha_1$ and $K\alpha_2$ components. Lp corrections were applied, but absorption corrections were ignored since for a spherical crystal with $\mu R=0{\cdot}58$ the maximum error in the relative structure amplitudes would be about 3% (*International Tables for X-ray Crystallography*, 1959).

3066 reflexions were measured within $2\theta=130°$ ($\sin\theta/\lambda=0{\cdot}588$ Å^{-1}) but only 2545 (83%) were observed above threshold. This represents 8·2 observations per parameter.

Table 1. *Crystal data*

$C_{21}H_{23}O_2Br$, F.W. 387·32, m.p. 100–101 °C
Space group: $P2_1/c$, $Z=4$
$a=6{\cdot}312$ (3), $b=15{\cdot}577$ (3), $c=18{\cdot}267$ (5) Å, $\beta=90{\cdot}99$ (3)°
$V=1795{\cdot}78$ Å^3
$D_x=1{\cdot}432$ g cm^{-3}
$D_m=1{\cdot}426$ g cm^{-3} (by flotation in KI solution at 23 °C)
$F(000)=800$, $\mu(\mathrm{Cu})=35{\cdot}11$ cm^{-1}

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Structure determination

The position of the Br atom was derived from a sharpened Patterson map, and all the other non-hydrogen atoms were located from an electron-density map phased on the Br atom. R for this trial structure was 0·24, assuming $B=4{\cdot}0$ Å^2 for all atoms.

Refinement was carried out by block-diagonal least-squares calculations with only the observed reflexions, minimizing the quantity $\sum w(|F_o|-|F_c|)^2$, where $w=1/\{1+[(|F_o|-40)/35]^4\}$ and $2{\cdot}1 \le |F_o| \le 157{\cdot}5$. After three cycles of refinement, R was reduced to 0·08, and the difference map computed at this stage revealed the positions of all the H atoms. Six more cycles with the H atoms included reduced R to a final value of 0·046 for the observed reflexions. In the final cycle, the maximum (shift/error) for the atomic parameters was 0·4, and the mean was 0·1. The final difference map showed no peaks higher than 0·2 e Å^{-3} except in the vicinity of the Br atom.

The atomic parameters and their estimated standard deviations as derived from the least-squares refinement are presented in Table 2. The structure factors for all measured reflexions are listed in Table 3. Only three reflexions of the observed category show high discrepancies. $10\bar{2}$, which is the strongest, appears to be affected by extinction and was excluded from the latter stages of refinement. The discrepancies of the 221 and $23\bar{1}$ are probably due to multiple diffraction. All unobserved reflexions have $|F_c| \le 1{\cdot}5|F_{\text{threshold}}|$.

All calculations were carried out with the NRC crystallographic computer programs by Ahmed, Hall, Pippy & Huber (1966). The scattering factor curves were those of Hanson, Herman, Lea & Skillman (1964) for C, O and Br, and of Stewart, Davidson & Simpson (1965) for H.

Discussion

A drawing of the molecular structure produced by Johnson's (1965) *ORTEP* program showing the 50% probability thermal ellipsoids is presented in Fig. 1. As predicted by Wiesner, the four-membered ring and the H atom on C(7) are *cis*. The bond lengths and valency angles, not corrected for thermal vibration, are given

Table 2. *Fractional coordinates, vibration tensor components* (Å^2) *for the expression* $T=\exp\,[-2\pi^2(U_{11}a^{*2}h^2+\ldots+2U_{23}b^*c^*kl+\ldots)]$, *and their e.s.d.'s* (*all* × 10^4)

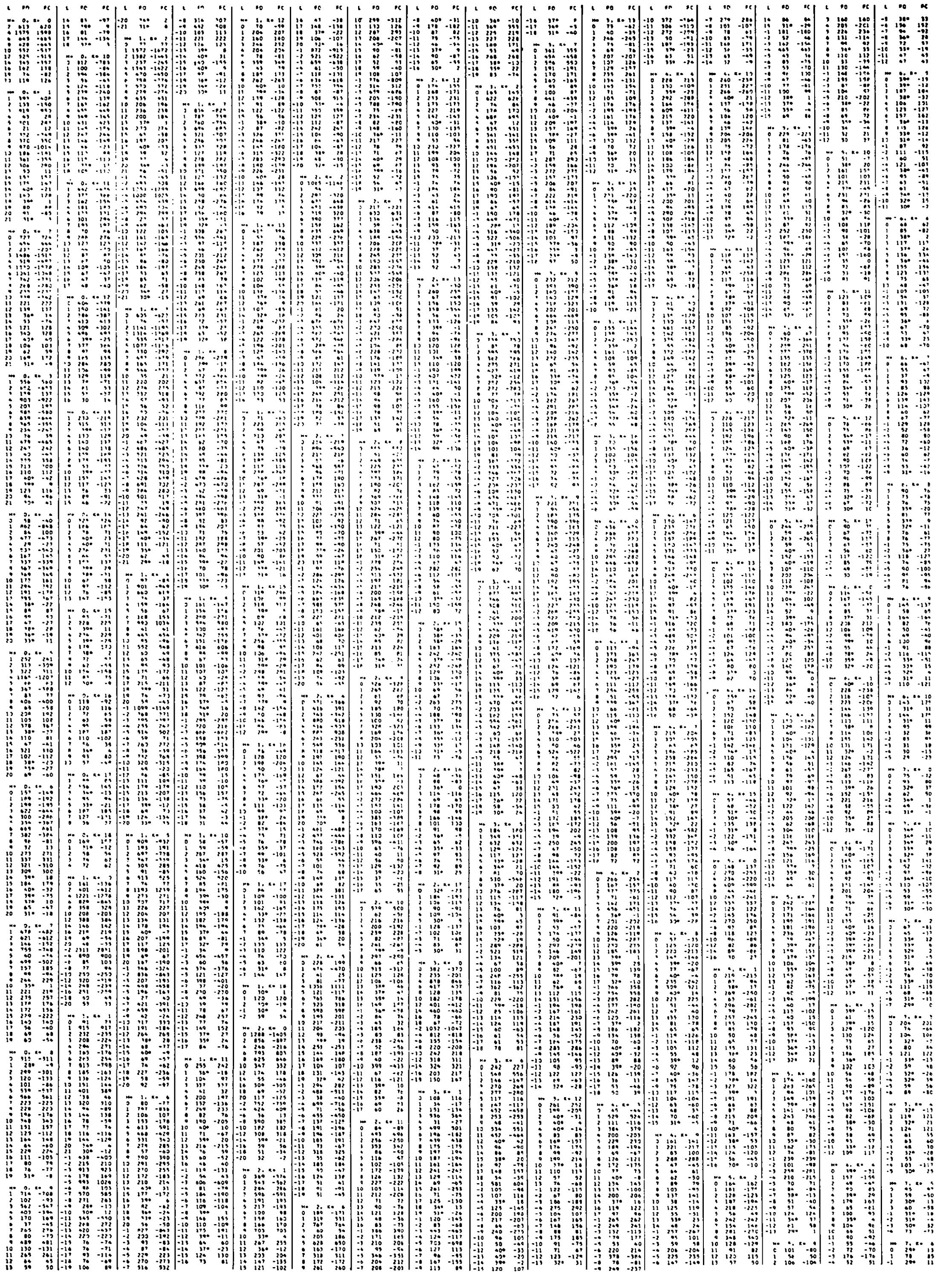
The isotropic temperature factors of the H atoms are in Å^2.

	x	y	z	U_{11}	U_{22}	U_{33}	$2U_{23}$	$2U_{13}$	$2U_{12}$
Br(1)	−2374 (1)	9491 (0)	−552 (0)	808 (3)	592 (2)	887 (3)	239 (6)	−300 (5)	429 (5)
O(1)	1817 (4)	5865 (1)	875 (1)	493 (14)	488 (14)	473 (14)	368 (23)	193 (22)	182 (22)
O(2)	4701 (4)	6271 (2)	283 (2)	485 (15)	578 (16)	914 (20)	489 (30)	433 (29)	198 (26)
C(1)	6138 (6)	3531 (3)	3281 (2)	625 (25)	568 (25)	559 (24)	183 (39)	−364 (40)	66 (40)
C(2)	5012 (6)	2699 (2)	3033 (2)	666 (26)	459 (22)	549 (24)	294 (37)	−30 (39)	13 (38)
C(3)	4577 (6)	2855 (2)	2217 (2)	526 (21)	327 (17)	461 (20)	−16 (30)	83 (33)	−21 (31)
C(4)	6525 (6)	3378 (2)	2003 (2)	404 (20)	578 (23)	548 (24)	157 (37)	177 (34)	84 (34)
C(5)	6152 (5)	4068 (2)	2580 (2)	442 (20)	429 (20)	536 (22)	195 (35)	−210 (33)	−199 (32)
C(6)	3870 (5)	4355 (2)	2404 (2)	407 (18)	334 (17)	355 (17)	39 (27)	−37 (28)	−100 (28)
C(7)	2814 (5)	3516 (2)	2108 (2)	391 (18)	356 (17)	336 (17)	7 (29)	98 (28)	−170 (29)
C(8)	2026 (5)	3536 (2)	1314 (2)	493 (21)	429 (20)	409 (19)	−66 (32)	−40 (32)	−178 (32)
C(9)	1083 (6)	4385 (2)	1074 (2)	532 (21)	524 (22)	353 (19)	−9 (33)	−187 (32)	−60 (35)
C(10)	2763 (5)	5063 (2)	1138 (2)	432 (19)	420 (18)	377 (19)	137 (30)	92 (30)	114 (31)
C(11)	3523 (5)	5185 (2)	1913 (2)	397 (18)	329 (17)	438 (19)	48 (29)	−19 (30)	−114 (28)
C(12)	1945 (5)	5493 (2)	2476 (2)	498 (20)	386 (18)	414 (19)	−131 (32)	−33 (31)	−17 (33)
C(13)	2665 (6)	4827 (2)	3021 (2)	680 (25)	447 (21)	363 (19)	−58 (32)	32 (35)	120 (36)
C(14)	431 (7)	6061 (3)	2478 (2)	749 (29)	643 (26)	515 (24)	−40 (40)	136 (41)	332 (44)
C(15)	2908 (5)	6393 (2)	453 (2)	436 (20)	377 (18)	335 (17)	20 (29)	36 (29)	−56 (29)
C(16)	1614 (5)	7149 (2)	228 (2)	421 (18)	355 (17)	252 (15)	−22 (27)	−94 (27)	−58 (28)
C(17)	2473 (5)	7749 (2)	−237 (2)	402 (19)	400 (18)	434 (19)	65 (30)	16 (31)	−78 (30)
C(18)	1318 (6)	8451 (2)	−467 (2)	608 (23)	402 (20)	448 (20)	183 (33)	−10 (35)	−104 (35)
C(19)	−715 (6)	8548 (2)	−225 (2)	537 (22)	400 (18)	426 (20)	−43 (32)	−191 (33)	96 (33)
C(20)	−1613 (5)	7961 (2)	239 (2)	443 (20)	546 (22)	419 (20)	26 (35)	−40 (32)	101 (34)
C(21)	−433 (5)	7261 (2)	464 (2)	464 (20)	467 (20)	360 (19)	118 (32)	42 (30)	9 (32)

	x	y	z	B		x	y	z	B
H(1,1)	7665 (57)	3428 (23)	3432 (19)	4·9 (0·9)	H(9,1)	662 (48)	4352 (20)	586 (17)	3·2 (0·7)
H(1,2)	5361 (52)	3814 (21)	3673 (18)	3·7 (0·7)	H(9,2)	−100 (48)	4552 (20)	1391 (16)	3·2 (0·7)
H(2,1)	5947 (53)	2183 (22)	3087 (18)	4·3 (0·8)	H(10)	3909 (44)	4947 (18)	874 (15)	2·2 (0·6)
H(2,2)	3713 (52)	2618 (21)	3292 (18)	4·0 (0·8)	H(11)	4701 (46)	5519 (20)	1914 (16)	2·9 (0·6)
H(3)	4358 (47)	2343 (20)	1973 (16)	3·1 (0·7)	H(13,1)	1570 (55)	4546 (22)	3302 (18)	4·4 (0·8)
H(4,1)	7945 (55)	3089 (23)	2098 (19)	4·6 (0·8)	H(13,2)	3861 (60)	5132 (25)	3379 (21)	5·7 (1·0)
H(4,2)	6478 (50)	3602 (20)	1478 (17)	3·6 (0·7)	H(14,1)	−479 (60)	6152 (25)	2844 (21)	5·6 (1·0)
H(5)	6998 (48)	4534 (20)	2585 (17)	3·3 (0·7)	H(14,2)	−40 (62)	6416 (26)	2077 (21)	6·0 (1·0)
H(7)	1673 (47)	3373 (19)	2404 (16)	2·8 (0·7)	H(17)	3809 (52)	7655 (21)	−387 (18)	4·0 (0·8)
H(8,1)	3213 (48)	3424 (20)	1038 (16)	3·2 (0·7)	H(18)	1864 (60)	8852 (25)	−806 (21)	5·4 (0·9)
H(8,2)	1035 (48)	3091 (20)	1241 (16)	3·2 (0·7)	H(20)	−3102 (49)	8021 (20)	385 (17)	3·5 (0·7)
					H(21)	−1141 (51)	6861 (21)	740 (17)	3·5 (0·7)

Table 3. *Observed and calculated structure factors* (× 10)

Unobserved reflexions are marked with an asterisk.



in Fig. 2. The C–H bond lengths are in the range 0·89–1·10 Å, and their mean is 0·96 Å.

Bond lengths

The C–C bond lengths cover a wide range: 1·302 (6) Å for the C(12)=C(14) double bond, 1·373–1·381 (5) Å for the six aromatic bonds, 1·487 (5) Å for the C(16)–C(15) bond between the aromatic ring and carbonyl group, and 1·500–1·587 (5) Å for the 16 C(sp^3)–C(sp^3) bonds. The aromatic bonds are of nearly equal lengths, but their mean of 1·377 Å is significantly shorter than the average of 1·394 ± 0·005 Å given by Sutton (1965). The longest C–C single bond, C(6)–C(11) = 1·587 (4) Å, is shared by the six-membered ring *A* and the four-membered ring *D*, and the second longest, C(6)–C(7) = 1·560 (4) Å, by ring *A* and the five-membered ring *B*. The elongation of these two bonds is balanced by significant contraction of C(9)–C(10), C(10)–C(11) and C(12)–C(13) so that the overall mean of the C–C single bonds is maintained at 1·530 Å which is close to Sutton's (1965) average value of 1·537 ± 0·005 Å.

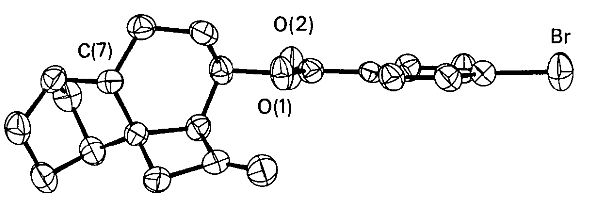


Fig. 1. Molecular structure of tetracyclic bromobenzoate showing thermal ellipsoids.

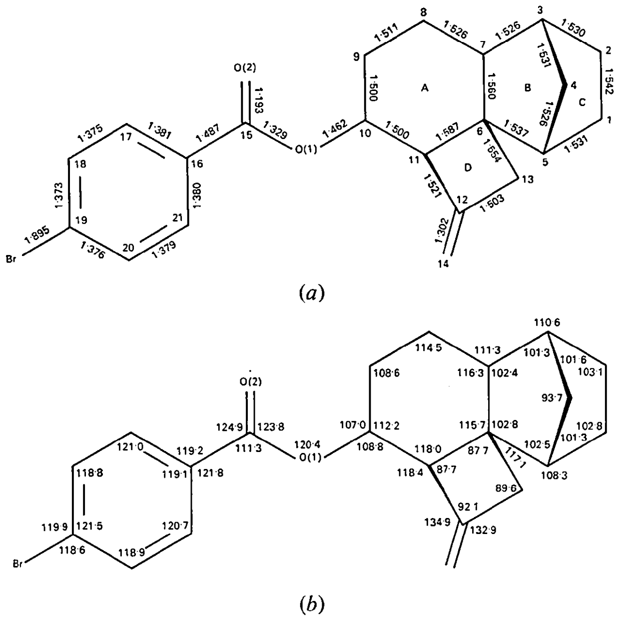


Fig. 2. (*a*) Bond lengths (Å) of tetracyclic bromobenzoate. The e.s.d.'s vary from 0·004 to 0·006 Å. (*b*) Valency angles (°). C(7)–C(6)–C(13) = 115·9, C(5)–C(6)–C(11) = 118·3°. The e.s.d. is 0·3°.

Valency angles

The smallest valency angles in the structure are the endocyclic angles of ring *D* (87·7–92·1°, mean = 89·3°). Consequently, the planar trigonal coordination at C(12) is achieved by a substantial increase in the angles C(11)–C(12)–C(14) and C(13)–C(12)–C(14) to 134·9 and 132·9°, respectively. Owing to the fusion of the rings, the tetrahedral coordination of the bonds at C(6) and C(11) becomes vastly distorted in each case, thus making some of the C–C–C angles as high as 118°. The C(3)–C(4)–C(5) angle at the bridging atom of the norbornane skeleton is 93·7° which agrees with the corresponding value in tetracyclic diketone (Przybylska, 1972).

Conformational analysis

Details of the mean planes through the rings and the carbonyl group are listed in Table 4. The torsion angles of rings *A*, *B* and *C* are presented in Table 5, where the signs are according to the convention of IUPAC–IUB Commission on Biological Nomenclature (1970), and the e.s.d.'s are 0·4° for ring *A* and 0·3° for the rest (Huber, 1961).

Table 4. *Mean planes*: $lX+mY+nZ=p$

(*a*) Parameters referred to Cartesian coordinates in Å

	l	m	n	p	χ^2
Benzene ring	−0·3306	−0·5198	−0·7877	−6·4509	0·1
Carbonyl group	−0·3067	−0·4967	−0·8119	−6·1789	0·7
Ring *A*	0·9331	−0·2119	−0·2905	−0·6954	65·6
Ring *B*	0·3028	0·1937	−0·9331	−2·0406	221·6
Ring *C*	0·8927	−0·3918	−0·2227	−0·1329	15·5
Ring *D*	−0·7821	−0·4989	−0·3734	−6·9477	2616·3

(*b*) Deviations from the mean planes (Å)

Benzene		Carbonyl		Ring *A*	
C(16)	0·000	C(16)	0·000	C(7)	0·011
C(17)	0·000	C(15)	0·002	C(8)	−0·014
C(18)	0·000	O(1)	0·000	C(10)	0·014
C(19)	0·000	O(2)	0·000	C(11)	−0·012
C(20)	0·000			C(9)*	−0·715
C(21)	0·000			C(6)*	0·190
Br*	0·049				
C(15)*	0·021				

Ring *B*		Ring *C*		Ring *D*	
C(3)	−0·022	C(3)	0·005	C(11)	−0·078
C(7)	0·026	C(2)	−0·009	C(12)	0·091
C(6)	−0·026	C(5)	−0·005	C(13)	−0·105
C(5)	0·023	C(1)	0·009	C(6)	0·072
C(4)*	0·874	C(4)*	0·876	C(14)*	0·395

* Identifies atoms excluded from the calculation.

The benzene ring is planar, and the adjacent Br and C(15) atoms are 0·05 and 0·02 Å from it. The four atoms of the carbonyl group form a plane nearly parallel to the benzene ring (Fig. 1).

The six-membered ring *A* has a distorted chair form which is considerably flattened at C(6). C(9) is −0·72 Å

Table 5. *Torsion angles*

Ring *A*	
C(6)—C(7)—C(8)—C(9)	−37·0°
C(7)—C(8)—C(9)—C(10)	61·6
C(8)—C(9)—C(10)-C(11)	−62·8
C(9)—C(10)-C(11)-C(6)	41·1
C(10)-C(11)-C(6)—C(7)	−16·1
C(11)-C(6)—C(7)—C(8)	13·6
Ring *B*	
C(7)-C(3)-C(4)-C(5)	58·0
C(3)-C(4)-C(5)-C(6)	−54·9
C(4)-C(5)-C(6)-C(7)	32·0
C(5)-C(6)-C(7)-C(3)	4·6
C(6)-C(7)-C(3)-C(4)	−39·5
Ring *C*	
C(4)-C(5)-C(1)-C(2)	−37·1
C(5)-C(1)-C(2)-C(3)	1·4
C(1)-C(2)-C(3)-C(4)	34·6
C(2)-C(3)-C(4)-C(5)	−56·1
C(3)-C(4)-C(5)-C(1)	57·0

from the plane calculated for C(7), C(8), C(10) and C(11), but C(6) is at a distance of only 0·19 Å. The torsion angles of C(6)–C(7) and C(6)–C(11) of −16·1 and 13·6° show that the highest strain occurs in these two bonds.

The torsion angles of the five-membered rings *B* and *C* are within 5° of the values for the maximally puckered envelope model for fused ring systems of Brutcher & Bauer (1962). C(4) is equidistant from the mean planes of the other four atoms of each of these two rings, but the four atoms of ring *B* are less planar than those of ring *C* (Table 4). The distortion of ring *B* seems to result from its fusion to ring *A* as found in tetracyclic diketone (Przybylska, 1972). The torsion angles of the norbornane system indicate the presence of *synchro*-twist (Altona & Sundaralingam, 1970), which is caused by the substitutions at C(6) and C(7). The torsion angle for C(5)–C(6) is 7·5° smaller than for C(3)–C(7), whereas the angle for C(1)–C(5) is 2·5° larger than for C(2)–C(3).

The deviation of the four-membered ring from planarity is considerable, as shown by the distances of the atoms from their mean plane (see ring *D* in Table 4). The diametrically opposite carbon atoms are situated on the same side of the plane and the torsion angles for the four bonds vary between 12·6 and 13·3°. These results agree with the distortion found in cyclobutane (Almenningen, Bastiansen & Skancke, 1961; Przybylska, 1958).

The packing of the molecules is shown in Fig. 3. There are no distances shorter than the sums of the appropriate van der Waals radii.

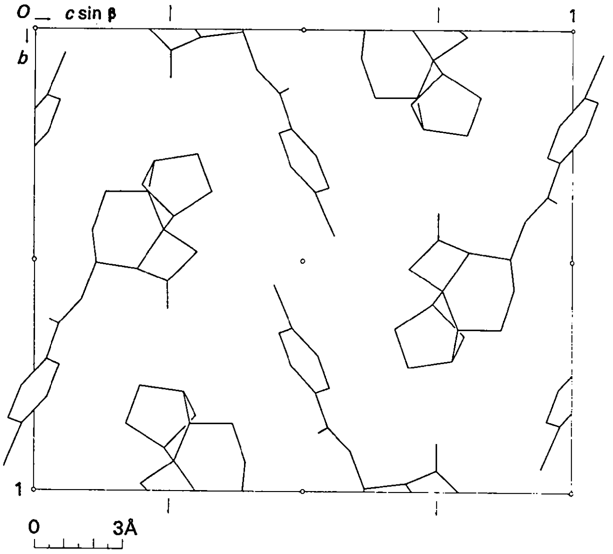


Fig. 3. Projection along the *a* axis showing packing of the molecules.

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References

Ahmed, F. R., Hall, S. R., Pippy, M. E. & Huber, C. P. (1966). NRC Crystallographic Programs for the IBM/360 System. *World List of Crystallographic Computer Programs*, 2nd ed., Appendix, p. 52. Utrecht: Oosthoek.

Almenningen, A., Bastiansen, O. & Skancke, P. N. (1961). *Acta Chem. Scand.* **15**, 711–712.

Altona, C. & Sundaralingam, M. (1970). *J. Amer. Chem. Soc.* **92**, 1995–1999.

Brutcher, F. V. Jr & Bauer, W. Jr (1962). *J. Amer. Chem. Soc.* **84**, 2233–2236.

Hanson, H. P., Herman, F., Lea, J. D. & Skillman, S. (1964). *Acta Cryst.* **17**, 1040–1044.

Huber, P. J. (1961). *Helv. Chim. Acta*, **44**, 2032–2033.

International Tables for X-ray Crystallography (1959). Vol. II, pp. 302–303. Birmingham: Kynoch Press.

IUPAC–IUB Commission on Biological Nomenclature (1970). *J. Mol. Biol.* **52**, 1–17.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794 revised, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Przybylska, M. (1958). *Acta Cryst.* **11**, 718–724.

Przybylska, M. (1972). *Acta Cryst.* B**28**, 2814–2820.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Sutton, L. E. (1965). *Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement*. London: The Chemical Society.

Wiesner, K., Poon, L., Jirkovský, I. & Fishman, M. (1969). *Canad. J. Chem.* **47**, 433–444.