and 0·958 (II). Scattering factors as in *SHELX*76. All calculations were performed on an IBM 43/41 computer.*

Discussion. The final atomic parameters are listed in Table 1. Fig. 1 shows a perspective view of the molecules of both modifications with the atomic numbering. The relevant bond lengths and bond angles are given in Table 2. There is good agreement between the corresponding values for the majority of bond angles and distances (within experimental error). There are some differences in the bonding around the C(2) atoms, induced by the *exo* S atom, just as in previously solved related structures (Stanković, Kapor, Ribár, Kálmán, Argay, Karanović, Stájer & Bernáth, 1985; Argay, Kálmán, Kapor, Stájer & Bernáth, 1985). Results for structures studied in this and the above papers are given in Table 3.

In accordance with the observations on the structures discussed by Argay *et al.* (1985), the 3,1-benzoxazine ring adopts an E_4 envelope conformation in both modifications. Puckering parameters (Cremer & Pople, 1975) and asymmetry factors (Kálmán, Czugler & Simon, 1982) for the benzoxazine five-membered rings *A* C(4a)–C(5)–C(9)–C(8)–C(8a) and *B* C(5)–C(6)–C(7)–C(8)–C(9) are given in Table 4.

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43805 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The molecules of the two crystal modifications are connected through hydrogen bonds of N–H···S type, to form dimers. The corresponding bond lengths and angles are: H···S = 2·45, N(1)···S = 3·391 (5) Å, ∠N–H···S = 145 (4)° (I); H···S = 2·27, N(1)···S = 3·317 (4) Å, ∠N–H···S = 163 (4)° (II). These data agree with the theoretical values for this type of bonding: N···S = 3·4, H···S = 3·1 Å (calc.), N···S = 3·4, H···S = 2·4 Å (obs.) (Hamilton & Ibers, 1968). The only substantial differences between the two modifications appear in the molecular packing in the crystal unit cell (Fig. 2).

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(–)-2-Bornyl 3-(9-Anthryl)propionate

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Abstract. $C_{27}H_{30}O_2$, $M_r = 386·5$, orthorhombic, $P2_12_12_1$, $a = 11·797$ (5), $b = 13·406$ (3), $c = 27·658$ (4) Å, $V = 4374·3$ Å^3, $Z = 8$, $D_x = 1·174$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 0·039$ mm^{-1}, $F(000) = 1664$, room temperature, $R = 0·086$ for 2506 observed reflections [$F_o > 2\sigma(F_o)$]. Each asymmetric unit contains two independent molecules, which are related by a pseudo centre of symmetry. The anthracene moieties are paired with their side groups opposed. There is an exceptionally

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small overlap between adjacent anthracene rings which are separated by a perpendicular distance of 3·54 (1) Å.

Introduction. The solid-state fluorescence spectrum of the title compound [henceforth (−)BAP] shows broad, structureless excimer emission typical of many anthracene derivatives but with an unusually large shift in the emission maximum from 21 000 cm^{-1} at 81 K to 22 400 cm^{-1} at 370 K (Hann, 1974). The solution behaviour of the excimer fluorescence is, however, normal (Rosseinsky, Hann & Brunner, 1976). After the nomenclature of Stevens (1962) anthracene derivatives have been classified (Cohen, Ludmer & Yakhot, 1975) into type A, which show monomer fluorescence, and types B_1 and B_2, which show excimer fluorescence. In type B_1 the anthracene moieties are arranged in infinite stacks with their side groups superimposed; in type B_2 the anthracene moieties are paired with the side groups opposed.

Cohen *et al.* (1975) have shown that the emission bands of stack structures (B_1) are more sensitive to changes in temperature than those in pair structures (B_2). It was shown that the temperature shift is related to a parameter γ, a function of the ratio of normal-mode frequencies of pairs of molecules in their ground and excited states. For a series of anthracene derivatives Cohen *et al.* (1975) found that the experimental data fitted well when γ was $\simeq 1$ for pair structures and when γ was $\simeq 3$ for stack structures. This means that the ratio of ground-state to excited-state frequencies is higher for pair than for stack structures. It was argued that this results from weaker intermolecular interactions in the ground state of the stack structures, probably owing to the repulsive contacts between molecular substituents. When Cohen *et al.* (1975) analysed Hann's data (Hann, 1974) for (−)BAP they obtained a value of $\gamma \simeq 3$ and predicted an intermolecular spacing of approximately 4 Å. They admitted, however, that the implied type B_2 stack structure was improbable on steric grounds. The present work was carried out to resolve this ambiguity.

Experimental. (−)BAP was prepared by the esterification of 3-(9-anthryl)propionic acid with (−)-borneol (Brewster & Ciotti, 1955). The 3-(9-anthryl)propionic acid was prepared according to the method of Daub & Doyle (1952). After chromatography on neutral alumina, (−)BAP was recrystallized from toluene/light petroleum as pale yellow/green prisms, m.p. 378–379 K. Elemental analysis, spectroscopic and optical rotation data were all satisfactory. Crystals suitable for X-ray analysis were grown from a hexane solution. Crystal size 0·27 × 0·34 × 0·42 mm, Stoe–Siemens AED diffractometer, cell parameters from $\pm\omega$ values of 16 reflections and their equivalents ($30 \le 2\theta \le 40°$), 3205 unique reflections measured by ω/θ scan, 2θ 3–45°, h 0 to 12, k 0 to 14, l 0 to 29, no absorption or extinction corrections, no significant intensity variation

Table 1. *Final positional* (× 10^4) *and equivalent isotropic thermal parameters* (Å² × 10^3)

$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	Molecule *A*				Molecule *B*			
	x	y	z	U_{eq}	x	y	z	U_{eq}
O(1)	−927 (5)	1043 (4)	5993 (2)	88 (2)	6028 (5)	3833 (5)	9012 (2)	128 (3)
O(2)	399 (4)	1991 (3)	5641 (2)	78 (2)	4409 (4)	3244 (4)	9257 (2)	86 (2)
C(1)	2672 (7)	3354 (5)	6705 (2)	72 (3)	2389 (6)	1652 (6)	8276 (3)	74 (3)
C(2)	3585 (7)	3971 (7)	6671 (3)	85 (3)	1438 (8)	1085 (7)	8332 (3)	90 (4)
C(3)	3820 (8)	4708 (6)	7010 (4)	94 (4)	1217 (8)	307 (7)	7990 (3)	93 (4)
C(4)	3081 (9)	4836 (6)	7392 (3)	94 (4)	1874 (7)	169 (6)	7612 (3)	78 (3)
C(5)	−207 (8)	3847 (7)	8325 (3)	88 (4)	5224 (9)	1118 (6)	6633 (2)	87 (4)
C(6)	−1132 (10)	3263 (8)	8392 (3)	102 (4)	6158 (8)	1678 (7)	6577 (3)	89 (4)
C(7)	−1425 (7)	2501 (6)	8054 (3)	84 (3)	6413 (8)	2422 (6)	6908 (3)	85 (3)
C(8)	−776 (7)	2356 (5)	7666 (3)	74 (3)	5746 (7)	2580 (5)	7312 (2)	72 (3)
C(9)	917 (7)	2805 (5)	7169 (2)	65 (3)	4062 (5)	2142 (4)	7806 (2)	44 (2)
C(10)	1442 (8)	4298 (5)	7850 (3)	73 (3)	3554 (7)	643 (5)	7129 (2)	73 (3)
C(11)	520 (8)	3704 (6)	7920 (2)	69 (3)	4523 (7)	1244 (5)	7051 (2)	64 (3)
C(12)	223 (7)	2933 (5)	7574 (2)	56 (3)	4761 (6)	1989 (5)	7398 (2)	55 (2)
C(13)	1890 (7)	3415 (5)	7102 (2)	60 (3)	3126 (6)	1514 (5)	7868 (2)	56 (2)
C(14)	2139 (7)	4162 (6)	7441 (3)	74 (3)	2854 (6)	751 (4)	7523 (2)	57 (3)
C(15)	663 (6)	2048 (5)	6785 (2)	64 (3)	4378 (6)	2949 (5)	8166 (2)	59 (2)
C(16)	−156 (6)	2461 (5)	6410 (2)	55 (2)	5146 (6)	2514 (5)	8563 (2)	67 (3)
C(17)	−310 (7)	1733 (5)	6001 (2)	57 (3)	5279 (6)	3239 (6)	8968 (2)	62 (3)
C(18)	481 (6)	1315 (5)	5216 (2)	65 (3)	4310 (6)	3975 (5)	9642 (2)	62 (3)
C(19)	1596 (7)	829 (5)	5193 (3)	68 (3)	3708 (5)	3514 (5)	10072 (2)	54 (2)
C(20)	1654 (6)	608 (5)	4635 (2)	67 (3)	3206 (6)	4427 (4)	10321 (2)	55 (2)
C(21)	1472 (11)	1668 (6)	4498 (3)	112 (4)	2586 (6)	4796 (4)	9877 (3)	67 (3)
C(22)	378 (9)	1935 (7)	4750 (3)	116 (4)	3528 (7)	4860 (5)	9499 (2)	82 (3)
C(23)	2509 (7)	1605 (8)	5237 (3)	117 (4)	2659 (6)	2989 (5)	9876 (3)	74 (3)
C(24)	2455 (11)	2188 (7)	4790 (4)	166 (7)	1851 (6)	3859 (6)	9741 (3)	90 (3)
C(25)	2764 (8)	169 (10)	4474 (5)	159 (6)	2464 (8)	4160 (6)	10762 (3)	99 (4)
C(26)	726 (8)	−111 (7)	4450 (3)	96 (4)	4093 (7)	5176 (5)	10507 (2)	76 (3)
C(27)	1707 (12)	−1 (6)	5540 (4)	145 (5)	4502 (8)	2836 (6)	10354 (3)	101 (4)

for four reflections measured every hour, reflection intensity decreased rapidly with increasing 2θ, 2510 reflections with $F_o > 2\sigma(F_o)$ were considered observed. Structure solved by multisolution direct methods, refined by blocked full-matrix least squares to minimize $\sum w\Delta^2$, $w^{-1} = \sigma^2(F_o) + 0{\cdot}0019(F_o)^2$. Anisotropic thermal parameters for all non-H atoms, H atoms in calculated positions with C–H = 1·08 Å, H–C–H = 109·5°, rigid methyl groups with freely refined orientation. Refined overall U_{iso}(H): benzene type 0·089; –CH, $-CH_2$ 0·066; $-CH_3$ 0·139 Å^2; R = 0·086, wR = 0·078 for 2506 reflections (four reflections probably suffering from extinction were removed), $(\Delta/\sigma)_{max} = 0{\cdot}56$, $(\Delta/\sigma)_{mean} < 0{\cdot}2$, $(\Delta\rho)_{max} = 0{\cdot}26$, $(\Delta\rho)_{min} = -0{\cdot}27$ e Å^{-3}. The relatively high R value may be explained by the rapid fall-off of intensity with increasing Bragg angle. Also, reflections 0*kl*, *k* odd, *h*0*l*, *l* odd and *hk*0, *h* odd at high Bragg angles were in most cases too weak to be considered observed owing to the presence of a pseudo centre of symmetry relating the two independent molecules. This resulted in only 4·6 reflections per refinable parameter. Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974). Program used: *SHELX* (Sheldrick, 1976).

Discussion. Final positional and equivalent isotropic thermal parameters are given in Table 1.* In view of the low reflection-to-parameter ratio (2506/548), owing to the rapid fall-off of intensity with increasing Bragg angle, the bond distances and angles given in Table 2 are normal within experimental error. Fig. 1, a projection of the two independent molecules (*A* and *B*) onto the best least-squares plane through the anthracene ring (atoms 1–14) in molecule *B*, illustrates the atom-labelling scheme used and shows the limited extent of overlap of the anthracene rings in molecules *A* and *B*. The conformational difference between the two independent molecules is shown in Fig. 2. They are rotational isomers, torsion angle C(14)–C(15)–C(16)–C(17) being 153 (1)° in molecule *A* and –151 (1)° in molecule *B*. A further conformational difference is due to a rotation of the bornyl moiety about bond O(2)–C(18). Torsion angles C(17)–O(2)–C(18)–C(19) and C(17)–O(2)–C(18)–C(22) are

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43827 (20 pp). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Bond distances* (Å) *and angles* (°) *in molecules A and B*

	A	*B*		*A*	*B*
C(1)–C(2)	1·361 (12)	1·363 (12)	C(15)–C(16)	1·521 (9)	1·538 (8)
C(1)–C(13)	1·436 (10)	1·436 (10)	C(16)–C(17)	1·505 (8)	1·491 (9)
C(2)–C(3)	1·390 (13)	1·431 (12)	C(17)–O(1)	1·176 (9)	1·195 (10)
C(3)–C(4)	1·379 (14)	1·316 (13)	C(17)–O(2)	1·348 (8)	1·301 (8)
C(4)–C(14)	1·438 (13)	1·416 (11)	O(2)–C(18)	1·486 (8)	1·453 (8)
C(5)–C(6)	1·356 (15)	1·343 (14)	C(18)–C(19)	1·470 (11)	1·516 (9)
C(5)–C(11)	1·423 (11)	1·431 (11)	C(18)–C(22)	1·540 (11)	1·555 (10)
C(6)–C(7)	1·428 (12)	1·388 (11)	C(19)–C(20)	1·573 (10)	1·524 (8)
C(7)–C(8)	1·332 (11)	1·383 (10)	C(19)–C(23)	1·503 (12)	1·524 (10)
C(8)–C(12)	1·432 (11)	1·427 (10)	C(19)–C(27)	1·476 (11)	1·519 (10)
C(9)–C(12)	1·398 (10)	1·411 (8)	C(20)–C(21)	1·487 (11)	1·503 (10)
C(9)–C(13)	1·422 (11)	1·400 (9)	C(20)–C(25)	1·503 (13)	1·543 (10)
C(9)–C(15)	1·501 (9)	1·518 (8)	C(20)–C(26)	1·546 (12)	1·538 (10)
C(10)–C(11)	1·362 (12)	1·415 (11)	C(21)–C(22)	1·510 (15)	1·529 (11)
C(10)–C(14)	1·411 (11)	1·375 (10)	C(21)–C(24)	1·575 (15)	1·544 (10)
C(11)–C(12)	1·451 (11)	1·415 (9)	C(23)–C(24)	1·466 (15)	1·551 (10)
C(13)–C(14)	1·404 (10)	1·436 (9)			
C(2)–C(1)–C(13)	121·8 (7)	120·9 (7)	C(16)–C(17)–O(1)	126·8 (6)	126·1 (6)
C(1)–C(2)–C(3)	122·9 (8)	118·8 (8)	C(16)–C(17)–O(2)	108·3 (6)	112·4 (6)
C(2)–C(3)–C(4)	118·6 (8)	121·3 (8)	O(1)–C(17)–O(2)	124·8 (6)	121·1 (6)
C(3)–C(4)–C(14)	118·9 (8)	122·8 (7)	C(17)–O(2)–C(18)	117·9 (5)	121·2 (5)
C(6)–C(5)–C(11)	120·9 (8)	120·1 (7)	O(2)–C(18)–C(19)	111·3 (6)	109·8 (5)
C(5)–C(6)–C(7)	121·2 (8)	120·2 (8)	O(2)–C(18)–C(22)	109·1 (6)	112·1 (5)
C(6)–C(7)–C(8)	119·5 (8)	121·4 (8)	C(19)–C(18)–C(22)	105·9 (6)	103·5 (5)
C(7)–C(8)–C(12)	122·5 (7)	120·9 (6)	C(18)–C(19)–C(20)	99·5 (6)	102·1 (5)
C(12)–C(9)–C(13)	120·5 (6)	118·2 (5)	C(18)–C(19)–C(23)	109·3 (6)	106·8 (5)
C(12)–C(9)–C(15)	122·3 (7)	119·0 (5)	C(18)–C(19)–C(27)	112·7 (8)	110·9 (6)
C(13)–C(9)–C(15)	117·6 (6)	122·8 (5)	C(20)–C(19)–C(27)	119·5 (6)	119·2 (5)
C(11)–C(10)–C(14)	120·2 (7)	123·6 (6)	C(23)–C(19)–C(27)	113·9 (8)	114·0 (6)
C(5)–C(11)–C(10)	120·8 (7)	121·5 (6)	C(20)–C(19)–C(23)	100·3 (6)	102·5 (5)
C(5)–C(11)–C(12)	118·0 (8)	121·2 (7)	C(19)–C(20)–C(21)	93·7 (6)	93·7 (5)
C(10)–C(11)–C(12)	121·1 (7)	117·3 (6)	C(19)–C(20)–C(25)	113·8 (7)	113·1 (5)
C(8)–C(12)–C(9)	123·9 (6)	121·9 (5)	C(19)–C(20)–C(26)	114·3 (6)	114·2 (6)
C(8)–C(12)–C(11)	117·8 (6)	116·1 (6)	C(21)–C(20)–C(25)	115·1 (8)	116·2 (6)
C(9)–C(12)–C(11)	118·3 (7)	122·0 (6)	C(21)–C(20)–C(26)	114·1 (7)	113·8 (5)
C(1)–C(13)–C(9)	125·9 (6)	119·8 (6)	C(25)–C(20)–C(26)	106·0 (7)	105·9 (5)
C(1)–C(13)–C(14)	114·6 (7)	118·6 (6)	C(20)–C(21)–C(22)	103·5 (7)	103·3 (6)
C(9)–C(13)–C(14)	119·4 (6)	121·5 (6)	C(20)–C(21)–C(24)	100·7 (8)	103·4 (5)
C(4)–C(14)–C(10)	116·5 (7)	124·8 (6)	C(22)–C(21)–C(24)	106·8 (7)	107·7 (6)
C(4)–C(14)–C(13)	123·1 (7)	117·3 (6)	C(18)–C(22)–C(21)	101·0 (7)	101·3 (5)
C(10)–C(14)–C(13)	120·4 (7)	117·9 (6)	C(19)–C(23)–C(24)	105·6 (8)	103·8 (5)
C(9)–C(15)–C(16)	111·3 (5)	110·1 (5)	C(21)–C(24)–C(23)	103·2 (8)	101·0 (6)
C(15)–C(16)–C(17)	110·6 (5)	110·6 (5)			

−112 (1) and 132 (1)° respectively in molecule *A*; and −147 (1) and 99 (1)° respectively in molecule *B*. The best least-squares planes through the anthracene moieties of the two molecules [which are planar to within 0·04 (1) Å] are separated by a perpendicular distance of 3·54 (1) Å.

The packing in the unit cell is illustrated in Fig. 3. It can be seen that the structure is of the paired or B_2 type, with the molecules stacking in the **b** direction. This is at variance with the analysis of Cohen *et al.* (1975) and the spacing of 3·54 (1) Å between the anthracene rings is shorter than their predicted value of 4 Å. The most probable cause of the anomaly in the fluorescence behaviour of (−)BAP is the exceptionally small lateral overlap between the adjacent anthracene rings, perhaps supplemented by large repulsive terms normally associated with stack-type structures (Yakhot, Cohen & Ludmer, 1979). This will cause weakening of the excimer interaction and thus explains the deviation from the normal series. The unexceptional behaviour of (−)BAP in solution is also explained, as the same constraints will not apply.

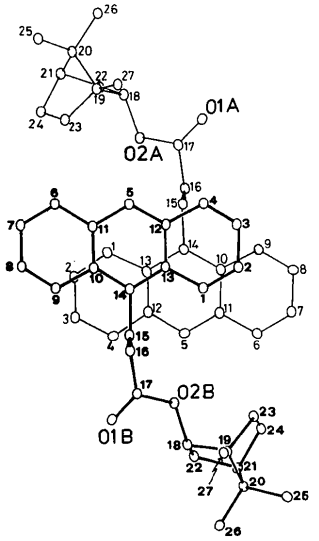

Fig. 1. Projection of molecules *A* and *B* onto the best least-squares planes through the anthracene moiety of molecule *B*.

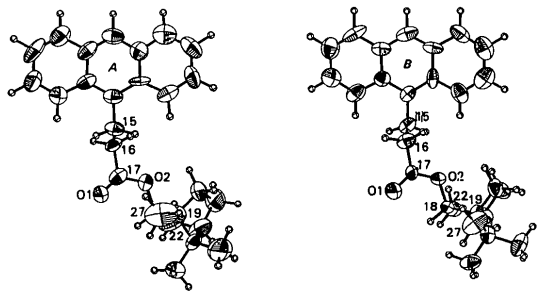

Fig. 2. Conformational differences between molecules *A* and *B* [*ORTEP*; Johnson (1976); vibrational ellipsoids at 50% probability level].

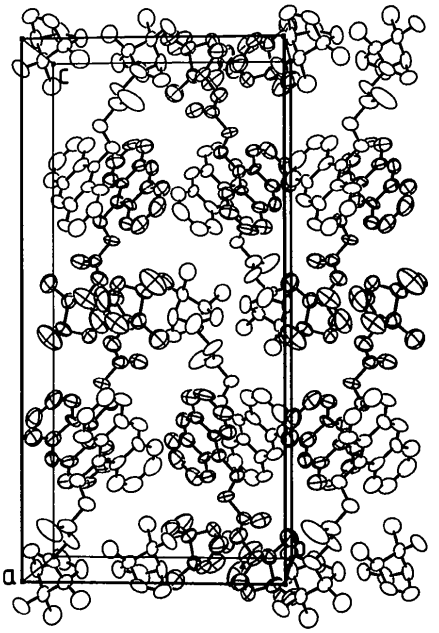

Fig. 3. Packing diagram (Johnson, 1976) viewed down **a**. ⊖ molecule *A*; ○ molecule *B*.

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