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The Crystal and Molecular Structure of *N*-(4-Bromobenzyl)isoquinolinium 4-Dithiocarboxylate. An Adduct of *N*-(4-Bromobenzyl)isoquinolinium Bromide and Carbon Disulphide

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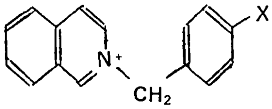
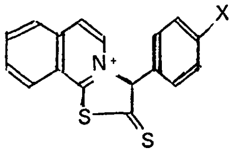
The crystal and molecular structure of *N*-(4-bromobenzyl)isoquinolinium 4-dithiocarboxylate, a novel adduct of *N*-(4-bromobenzyl)isoquinolinium bromide with carbon disulphide, has been determined. The crystals are triclinic, space group $P\bar{1}$, with two molecules of the adduct, and two dimethylformamide molecules of crystallization per unit cell. Cell dimensions are $a=8{\cdot}435$ (17), $b=10{\cdot}880$ (21), $c=12{\cdot}870$ (25) Å, $\alpha=113{\cdot}18$ (8), $\beta=111{\cdot}44$ (8), $\gamma=83{\cdot}33$ (9). The structure was determined by Patterson and heavy atom methods, and refined to a residual of 8·5% for reflections with $I>2\sigma(I)$. The dithiocarboxylate group, which is planar, is inclined at 71·6° to the isoquinolinium ring system, and has carbon–sulphur bond lengths of 1·693 (10) Å and 1·649 (10) Å. The dimethylformamide molecule is also planar. The dihedral angle between the isoquinolinium and bromobenzyl ring planes is 108·5°.

Introduction

The reaction of *N*-benzylisoquinolinium bromides (I) with carbon disulphide in strongly basic aqueous dioxane yields adducts which are 3-phenylthiazolo-[2,3-*a*]isoquinolinium-2-thione betaines (II) (Kröhnke & Steuernagel, 1961; Baldwin, McDaniel, Newton & Paul, 1966; Newton, McDaniel, Baldwin & Paul, 1967).



(I)



(II)

In studies directed toward understanding the mechanism of the cycloaddition process Baldwin & Duncan (1971*a*,*b*) subjected a series of *N*-benzylisoquinolinium salts to the above mentioned reaction conditions and isolated a number of representatives of a new class of adduct, not previously examined.

Initial studies of the new adducts by mass spectrometric and by spectral techniques did not lead to an unequivocal structure determination, and it was therefore decided to resort to an X-ray analysis. The product chosen for the X-ray structure determination was an adduct from *N*-(4-bromobenzyl)isoquinolinium bromide (I, X = 4′-Br) and was found to be an *N*-benzylisoquinolinium 4-dithiocarboxylate. The schematic formula of the new adduct, hereafter referred to as NBID, and the numbering used in this study, are shown in Fig. 1.

Experimental

Crystals of NBID, grown from *N*,*N*-dimethylformamide–acetonitrile were deep-red laths of variable habit. Weissenberg and precession photographs revealed no symmetry axes, and the triclinic unit cell with parameters given in Table 1 was therefore adopted. Using the assumed molecular formula and the observed density (Table 1), the number of molecules per unit cell was calculated to be 2·5, which was clearly impossible. Since the chemical data available at the time ruled against a substantial error in the molecular weight, the cause of this discrepancy was not obvious, and in fact it was subsequently shown that the unit cell also contained two molecules of dimethylformamide (DMF), the crystallizing solvent.

Table 1. *Crystallographic data*

Unit-cell dimensions	$a=$ 8·435 (17) Å
	$b=$ 10·880 (21)
	$c=$ 12·870 (25)
	$\alpha=$ 113·18 (8)°
	$\beta=$ 111·44 (8)
	$\gamma=$ 83·33 (9)
	$V_c=$ 1010·1 Å^3
Space group	$P\bar{1}$
Two NBID and two dimethylformamide molecules per cell	
Density (calculated)	1·471 g cm^{-3}
Density (observed)	1·469 (5) g cm^{-3}
Absorption coefficient (Mo $K\alpha$)	23·5 cm^{-1}

The lattice constants were determined by centering 32 reflections and subsequent least-squares refinement. In this and in all tables the standard deviation in the last place is shown in parentheses.

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An initial set of data including the levels $0kl$ through $4kl$ was collected by eye-estimation of Weissenberg photographs taken using Cu $K\alpha$ radiation. This sufficed for the initial structure determination, but was subsequently discarded in favor of a more accurate set of data collected with a card-controlled Enraf–Nonius three-circle diffractometer operated in a θ–2θ peak scan mode.

Filtered Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å) was used, data being collected to $\sin\theta/\lambda = 0{\cdot}66$ Å^{-1}, *i.e.*, equivalent to the observable limit for Cu $K\alpha$ radiation. Total counting time per reflection was about 50 s. Of a possible 4042 reflections, 2683 were observed to have $I > 2\sigma(I)$. The crystal used for data collection measured $0{\cdot}15 \times 0{\cdot}30 \times 0{\cdot}6$ mm, the long dimension being along the φ axis. No correction was made for absorption.

Structure determination

It was not known at the outset whether the space group was $P1$ or $P\bar{1}$. Rather than attempt to decide between the two alternatives with statistical methods, which might have been unreliable in the presence of the heavy bromine atoms (Sim, 1958), our approach was to calculate the Patterson function and to look for the bromine–bromine, sulphur–sulphur and bromine–sulphur peaks. If an internally consistent interpretation could be made of all the major Patterson peaks in terms of the vectors generated by this set of three atoms, then not only would their coordinates be revealed, but also the space-group ambiguity be resolved. This in fact proved to be the case. Inspection of the Patterson function calculated using the eye-estimated intensities suggested that the space group

Table 2. *Fractional coordinates* $\times 10^4$

The thermal parameters, $B_{ij} \times 10^4$, are the coefficient in the expression $\exp\left[-\sum B_{ij}h_ih_j\right]$.

	x	y	z	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Br	1906 (2)	1335 (1)	1024 (1)	284 (2)	149 (1)	75 (1)	44 (2)	76 (2)	−57 (3)
S(1)	−1398 (3)	4811 (3)	7059 (2)	98 (3)	138 (3)	124 (2)	100 (4)	88 (5)	8 (5)
S(2)	−0302 (3)	2775 (3)	8198 (3)	148 (4)	153 (3)	160 (3)	149 (5)	145 (6)	−26 (6)
N(1)	4173 (7)	3168 (6)	7165 (5)	91 (10)	113 (7)	64 (5)	55 (10)	83 (12)	34 (14)
C(1)	2777 (11)	1573 (8)	2677 (7)	169 (15)	89 (8)	69 (6)	48 (12)	118 (17)	52 (18)
C(2)	2225 (12)	0714 (8)	3038 (8)	175 (16)	88 (9)	87 (8)	−6 (13)	85 (19)	−67 (19)
C(3)	2873 (11)	0873 (8)	4226 (8)	168 (16)	86 (8)	100 (8)	44 (13)	144 (19)	40 (19)
C(4)	4090 (10)	1899 (8)	5069 (7)	111 (13)	101 (9)	79 (7)	49 (13)	106 (16)	55 (17)
C(5)	4575 (11)	2723 (9)	4668 (8)	121 (14)	117 (10)	89 (8)	52 (14)	44 (17)	−36 (19)
C(6)	3928 (11)	2593 (8)	3484 (8)	147 (15)	103 (9)	93 (8)	64 (14)	68 (18)	−35 (19)
C(7)	4863 (10)	2002 (9)	6365 (8)	124 (14)	123 (10)	79 (7)	61 (14)	97 (17)	97 (19)
C(8)	2525 (9)	3059 (8)	7108 (6)	85 (11)	105 (9)	58 (6)	37 (12)	56 (14)	6 (15)
C(9)	1833 (9)	4079 (8)	7818 (6)	89 (11)	101 (8)	61 (6)	41 (11)	64 (14)	−6 (15)
C(10)	2832 (9)	5257 (7)	8642 (6)	126 (13)	83 (7)	50 (5)	23 (10)	75 (14)	0 (16)
C(11)	4516 (9)	5331 (7)	8687 (7)	111 (12)	78 (7)	69 (6)	69 (11)	41 (14)	−26 (15)
C(12)	5138 (9)	4260 (9)	7932 (7)	96 (12)	132 (10)	75 (7)	92 (14)	65 (15)	−17 (17)
C(13)	0045 (9)	3864 (8)	7699 (7)	103 (12)	93 (8)	66 (6)	−1 (12)	76 (15)	−4 (16)
C(14)	2233 (11)	6341 (9)	9454 (7)	138 (14)	114 (10)	73 (7)	72 (13)	30 (16)	−20 (19)
C(15)	3302 (14)	7428 (9)	10267 (8)	259 (22)	90 (9)	74 (7)	18 (13)	65 (21)	−56 (23)
C(16)	4992 (13)	7481 (9)	10306 (9)	212 (20)	101 (10)	118 (10)	83 (16)	37 (23)	−99 (23)
C(17)	5597 (12)	6477 (9)	9541 (8)	180 (17)	118 (10)	85 (7)	87 (14)	14 (19)	−130 (21)
O(1)	7670 (15)	0123 (9)	3750 (10)	485 (30)	151 (10)	233 (13)	172 (19)	412 (35)	82 (28)
N(2)	8242 (11)	1835 (7)	3402 (7)	212 (16)	110 (9)	104 (7)	61 (13)	105 (18)	−18 (19)
C(18)	8248 (15)	1243 (11)	4096 (10)	278 (24)	143 (12)	121 (10)	100 (19)	218 (28)	48 (28)
C(19)	8901 (21)	3172 (12)	3855 (12)	455 (40)	140 (14)	170 (15)	110 (23)	342 (43)	3 (37)
C(20)	7605 (20)	1127 (17)	2088 (17)	303 (31)	307 (26)	107 (11)	159 (28)	32 (31)	−173 (46)

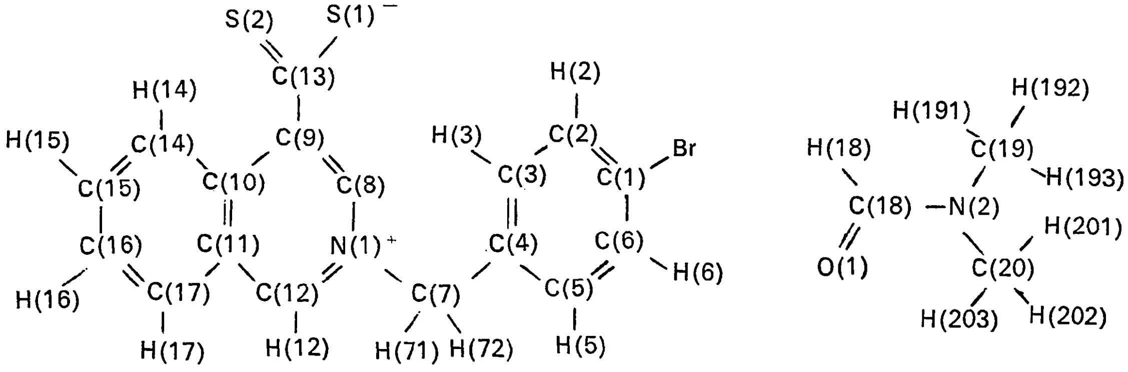


Fig. 1. Molecular formula and atomic numbering.

was $P\bar{1}$, and provided starting coordinates for Br, S(1) and S(2).

A Fourier synthesis, phased on these atoms in the usual way, immediately revealed the remainder of the molecular skeleton. A difference Fourier, subtracting out the NBID molecule was relatively featureless in the vicinity of the assumed atomic sites, but had in the asymmetric unit four peaks clustered together, and in positions suggestive of a molecule of dimethylformamide. Including one such molecule in the moleculaı weight per asymmetric unit, the discrepancy between the observed and calculated densities was eliminated (Table 1). After several cycles of refinement with an overall isotropic temperature factor, the reliability index for the photographically measured data remained above 30%, which was rather unsatisfactory, and it was decided to re-collect the data with a diffractometer, as described above. All subsequent discussion will refer to the diffractometer data.

Block-diagonal refinement with isotropic temperature factors led to a residual of 16% for the new data set. Introduction of anisotropic thermal parameters further reduced R to 9·3%. At this stage a difference Fourier map was calculated using the low-angle data ($\sin \theta/\lambda = 0{\cdot}32$ Å^{-1}) and revealed peaks at or near all the expected hydrogen positions with the exception of those associated with the dimethylformamide molecule, which apparently undergoes rather large thermal motion. The hydrogen atoms were placed at stereochemically reasonable positions, and included in the refinement with isotropic thermal factors. All atoms were then further refined to convergence, the final R value for the reflections with $I > 2\sigma(I)$ being 8·5%. The weighting scheme was similar to that described by Stout & Jensen (1968) for diffractometer data. The final parameters for the non-hydrogen atoms are given

Table 3. *Fractional hydrogen coordinates* ($\times 10^3$) *and thermal parameters* (Å^2)

	x	y	z	B
H(2)	143 (15)	014 (11)	244 (10)	1·9 (25)
H(3)	258 (14)	037 (10)	472 (10)	3·0 (25)
H(5)	541 (14)	346 (11)	527 (10)	4·5 (25)
H(6)	428 (14)	313 (10)	312 (9)	5·4 (23)
H(71)	486 (14)	131 (10)	655 (9)	5·0 (23)
H(72)	597 (14)	200 (10)	671 (9)	6·7 (23)
H(8)	189 (13)	214 (9)	657 (9)	0·0 (20)
H(12)	613 (13)	436 (10)	795 (9)	5·8 (21)
H(14)	112 (12)	630 (9)	932 (8)	3·4 (19)
H(15)	267 (13)	839 (10)	1075 (9)	3·1 (22)
H(16)	522 (15)	831 (11)	1053 (10)	8·5 (26)
H(17)	668 (15)	636 (10)	958 (10)	6·7 (25)
H(18)	837 (16)	163 (12)	470 (11)	4·0 (28)
H(191)	900 (19)	369 (14)	473 (13)	5·6 (35)
H(192)	952 (19)	330 (14)	330 (13)	14·1 (35)
H(193)	779 (18)	374 (13)	351 (13)	9·5 (35)
H(201)	691 (19)	168 (14)	157 (13)	13·7 (35)
H(202)	846 (19)	121 (14)	163 (13)	10·3 (36)
H(203)	678 (19)	100 (14)	183 (13)	4·9 (36)

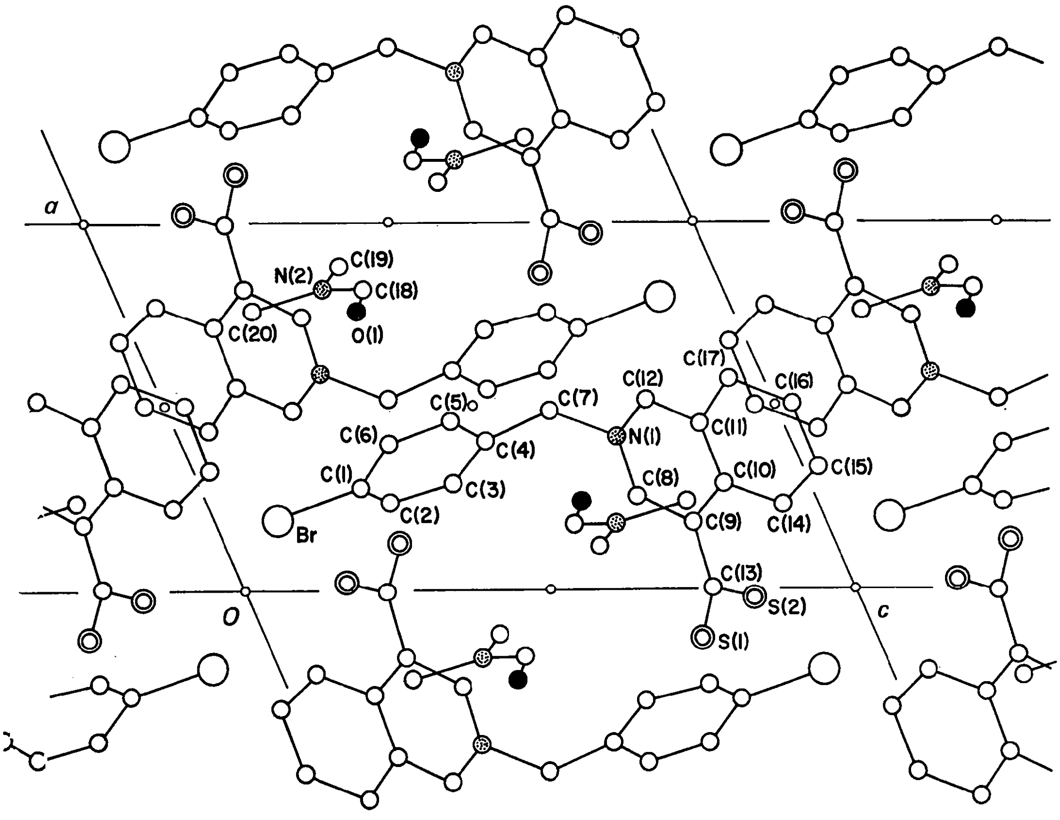


Fig. 2. Molecular packing

Table 4. *Observed and calculated structure factors* (× 10)

Table 4 (*cont.*)

H	FO	FC
K= 8, L= 4		
0	145	-107
-1	0*	11
-2	107	137
-3	43*	40
-4	30*	-16
-5	119	-131
-6	36*	-23
K= -8, L= 4		
0	71	74
0	75	74
1	24*	-23
2	79	102
3	13*	10
4	79	94
5	32*	-42
6	87	89
-1	262	308
-2	162	172
-3	167	164
-4	151	-145
-5	150	-163
-6	110	102
-7	101	97
-8	48*	64
K= 9, L= 4		
0	81	-76
1	40*	67
2	55*	76
3	0*	-12
0	79	-70
-1	97	-93
-2	44*	4
-3	31*	-4
-4	53*	10
-5	23*	34
K= -9, L= 4		
0	60	-61
0	63	-91
1	129	-145
2	93	-203
3	57	44
4	62	77
5	0*	46
6	117	-127
-1	61	92
-2	126	134
-3	96	116
-4	63	-73
-5	26*	43
-6	66	46
-7	49*	46
K= 10, L= 4		
0	41*	11
1	95	102
0	36*	11
-1	51*	-39
-2	33*	27
-3	65	53
K= -10, L= 4		
0	0*	35
0	44*	35
1	14*	-4
2	66	-73
3	73	-73
4	44*	-33
5	23*	4
-1	0*	-6
-2	0*	-27
-3	138	-143
-4	114	-132
-5	36*	21
-6	44	42
K= -11, L= 4		
0	28*	-21
0	42*	-21
1	94	91
2	11*	27
3	0*	7
4	0*	-2
K= -11, L= 4		
-1	54	-50
-2	44*	-43
-3	49*	16
-4	0*	15
-5	16*	11
K= -12, L= 4		
0	109	100
0	114	100
1	37	8
2	54	45
3	57	-32
K= -12, L= 4		
-1	29*	-8
-2	0*	-14
-3	0*	-34
-4	56	54
K= -13, L= 4		
0	70	-65
0	70	-65
K= -13, L= 4		
-1	43*	-26
K= 0, L= 5		
0	452	-460
1	142	-147
2	434	441
3	356	357
4	119	126
5	143	-137
6	136	165
7	72	-81
0	451	-460
-1	170	138
-2	362	374
-3	452	464
-4	252	251
-5	212	-210
-6	201	-187
-7	44	-62
-8	0*	-16
-9	37*	-4
-10	0*	-15
K= 1, L= 5		
0	47	-44
1	314	334
2	81	73
3	46	44
4	305	-311
5	0*	-34
6	13*	-2
7	117	113
0	90	-49
-1	503	-543
-2	90	-122
-3	44	-32
-4	65	-53
-5	230	-216
-6	161	-153
-7	45	54
-8	0*	35
-9	0*	-11
-10	73	-91
K= -1, L= 5		
0	174	-152
0	170	-152
1	500	-561
2	0*	-23
3	196	195
4	112	106
5	203	-225
6	160	-186
7	55*	62
-1	647	619
-2	340	342
-3	15*	3
-4	142	-161
-5	163	-157
-6	170	169
-7	240	251
-8	158	153
-9	13*	7
-10	30*	-72
K= 2, L= 5		
0	124	-124
1	225	217
2	187	187
3	213	-227
4	219	-229
5	0*	-12
6	42*	0
7	32*	15
0	121	-128
-1	520	-526
-2	539	-560
-3	153	148
-4	364	404
-5	350	349
-6	230	-233
-7	216	-226
-8	13*	-1
-9	60	79
K= -2, L= 5		
0	12*	-29
0	24*	-23
1	606	-641
2	361	-366
3	172	174
4	281	290
5	60	51
6	135	-141
7	30*	-27
-1	403	403
-2	188	187
-3	215	-203
-4	272	-279
-5	31*	-27
-6	69	84
-7	33*	43
-8	56	49
-9	51	-76
-10	125	111
K= 3, L= 5		
0	421	424
1	473	462
2	77	64
3	303	-315
4	96	-111
5	94	91
6	131	141
0	422	424
-1	123	131
-2	133	-182
-3	51	-41
-4	166	165
-5	142	140
-6	139	141
-7	66	53
-8	43*	41
-9	23*	13
K= -3, L= 5		
0	560	563
0	553	563
1	194	206
2	342	-347
3	59	-61
4	14*	5
5	116	130
6	20*	-9
7	16*	27
-1	177	177
-2	263	-274
-3	481	-531
-4	467	-535
-5	23*	-5
-6	148	195
-7	32*	17
-8	177	-198
-9	121	-123
-10	47*	-52
K= 4, L= 5		
0	94	94
1	17*	16
2	118	-124
3	0*	3
4	36*	60
5	104	100
6	0*	21
0	95	94
-1	36*	26
-2	139	-158
-3	142	-157
-4	11*	24
-5	64	61
-6	16*	-41
-7	120	-127
-8	66	-77
-9	73	-91
K= -4, L= 5		
0	378	344
0	376	344
1	104	-102
2	249	-245
3	43	-37
4	165	175
5	117	122
6	86	49
7	52*	-48
-1	512	526
-2	122	54
-3	156	-158
-4	162	167
-5	297	336
-6	72	83
-7	89	-92
-8	159	-164
-9	61	57
K= 5, L= 5		
0	272	275
1	244	-262
2	227	-240
3	105	-110
4	126	127
5	32*	50
0	268	275
-1	144	140
-2	42*	8
-3	237	-236
-4	146	-153
-5	56	-49
-6	50	45
-7	46*	16
-8	75	69
K= -5, L= 5		
0	165	124
0	111	128
1	363	429
2	77	88
3	244	-269
4	156	-166
5	57	-34
6	42*	12
7	31*	15
-1	127	-134
-2	243	-301
-3	204	-233
-4	233	260
-5	277	315
-6	207	238
-7	0*	33
-8	0*	12
-9	81	82
K= 6, L= 5		
0	222	-239
1	127	-129
2	65	-53
3	107	125
4	95	91
5	24*	-9
0	220	-239
-1	242	265
-2	177	195
-3	41*	25
-4	45	-62
-5	38*	55
-6	52	75
-7	31*	20
-8	0*	2
K= -6, L= 5		
0	294	-329
0	302	-329
1	0*	-4
2	56	63
3	63	-80
4	45	-64
5	0*	-3
6	38*	19
7	0*	-19
-1	296	-354
-2	153	-163
-3	84	92
-4	60	65
-5	135	-133
-6	324	-336
-7	194	-207
-8	0*	21
-9	77	93
K= 7, L= 5		
0	17*	-24
1	0*	-30
2	20*	1
3	54	48
4	0*	6
0	39*	-28
-1	0*	38
-2	96	112
-3	20*	-15
-4	67	-56
-5	75	-65
-6	24*	-34
-7	43*	63
K= -7, L= 5		
0	64	-69
0	73	-69
1	115	122
2	270	249
3	116	122
4	59	-56
5	57	-71
6	43*	23
-1	94	-107
-2	64	78
-3	65	73
-4	43*	46
-5	40*	-16
-6	45	40
-7	124	-139
-8	0*	33
-9	82	-85
K= 8, L= 5		
0	36*	-43
1	49*	40
2	56	77
3	54	61
0	57	-43
-1	102	-122
-2	0*	-15
-3	73	75
-4	24*	21
-5	0*	34
-6	0*	-10
K= -8, L= 5		
0	57	-53
0	44	-53
1	153	-174
2	53	64
3	111	122
4	0*	28
5	0*	-12
6	43*	-13
-1	65	43
-2	133	162
-3	222	261
-4	43	43
-5	25*	21
-6	136	-157
-7	114	108
-8	71	72
K= 9, L= 5		
0	24*	11
1	41*	5
0	0*	11
-1	74	-62
-2	45*	-40
-3	0*	92
-4	31*	17
K= -9, L= 5		
0	0*	-41
0	0*	-41
1	51	-56
2	111	-118
3	27*	1
4	18*	-22
5	33*	-3
-1	56	64
-2	0*	-15
-3	183	-184
-4	91	-100
-5	41*	-14
-6	89	80
-7	95	92
K= -10, L= 5		
0	52	30
0	19*	30
1	91	-96
2	120	-120
3	33*	-4
4	67	64
5	37*	41
K= -10, L= 5		
-1	144	156
-2	35*	54
-3	62	-94
-4	101	-117
-5	65	-66
-6	23*	1
-7	52*	-28
K= -11, L= 5		
0	41*	62
0	75	62
1	66	22
2	39*	20
3	17*	5
4	0*	24
K= -11, L= 5		
-1	34*	48
-2	53	-38
-3	0*	-30
-4	0*	-20
-5	87	72
-6	65	46
K= -12, L= 5		
0	83	86
0	100	86
1	0*	-24
2	17*	-19
3	63	-41
K= -12, L= 5		
-1	0*	-2
-2	45*	10
-3	55	-29
-4	97	81
K= -13, L= 5		
0	84	-87
0	77	-87
K= -13, L= 5		
-1	24*	-25
-2	51*	-70
K= 0, L= 6		
0	133	-142
1	216	209
2	660	665
3	0*	2
4	170	-190
5	184	-175
6	34*	7
7	54*	42
0	137	-142
-1	648	-536
-2	185	-170
-3	560	527
-4	240	297
-5	127	127
-6	95	-82
-7	52	-35
-8	97	109
-9	0*	-27
-10	27*	-27
K= 1, L= 6		
0	92	35
1	404	386
2	167	239
3	167	-166
4	35*	-27
5	74	85
6	105	129
0	34*	35
-1	497	-490
-2	161	134
-3	281	305
-4	267	254
-5	238	-239
-6	24*	7
-7	254	-254
-8	35*	7
-9	35*	46
K= -1, L= 6		
0	475	-467
0	473	-469
1	117	-125
2	116	-149
3	147	154
4	129	-133
5	95	107
6	137	-143
7	0*	-4
-1	116	-79
-2	559	524
-3	341	327
-4	135	-139
-5	254	-245
-6	266	-263
-7	176	175
-8	237	211
-9	129	139
-10	56*	41
K= 2, L= 6		
0	127	135
1	345	353
2	61	-59
3	236	-263
4	42	-99
5	53	-41
6	0*	13
6	115	135
-1	351	-360
-2	586	-574
-3	130	-106
-4	87	74
-5	135	133
-6	156	-162
-7	47*	13
-8	93	-91
-9	0*	4
K= -2, L= 6		
0	570	-533
0	564	-530
1	140	-133
2	37*	14
3	255	261
4	80	96
5	113	-126
6	20*	7
7	0*	-46
-1	54	58
-2	178	171
-3	81	-96
-4	148	-136
-5	204	-204
-6	52	-56
-7	95	96
-8	114	-130
-9	83	-89
-10	136	-127
K= 3, L= 6		
0	213	224
1	53	47
2	271	-292
3	135	-146
4	49*	50
5	120	117
6	59	22
0	208	224
-1	206	198
-2	133	-132
-3	73	-78
-4	62	53
-5	104	106
-6	67	71
-7	33*	-8
-8	0*	6
-9	54*	52
K= -3, L= 6		
0	0*	34
0	0*	34
1	256	-285
2	125	-143
3	32*	24
4	239	222
5	32*	48
6	75	53
7	0*	-11
-1	557	576
-2	179	184
-3	37*	37
-4	255	-282
-5	205	-213
-6	46	40
-7	0*	-16
-8	64	73
-9	12*	-15
-10	76	-82
K= 4, L= 6		
0	213	213
1	37	-88
2	164	-179
3	94	115
4	67	67
5	80	57
0	211	213
-1	401	425
-2	47	13
-3	212	-223
-4	137	-110
-5	113	115
-6	199	204
-7	61	92
-8	40*	-46
-9	76	-49
K= -4, L= 6		
0	773	833
0	791	833
1	214	-219
2	62	-59
3	67	-59
4	103	117
5	43*	6
6	51*	-71
7	0*	-23
-1	135	145
-2	236	-236
-3	291	-334
-4	292	295
-5	314	350
-6	258	320
-7	62	93
-8	34*	6
-9	86	-90
-10	76	75
K= 5, L= 6		
0	77	73
1	237	-268
2	100	-114
3	0*	0
4	128	142
5	41*	27
0	78	73
-1	5*	-18
-2	156	171
-3	53	-68
-4	119	-127
-5	122	-150
-6	59	-49
-7	0*	-19
-8	78	-62
K= -5, L= 6		
0	16	16
0	31*	15
1	221	236
2	312	-339
3	247	-247
4	177	-185
5	95	105
6	77	65
7	27*	6
-1	46	36
-2	324	-329
-3	135	-164
-4	113	-117
-5	31*	14
-6	64	-70
-7	0*	-3
-8	24*	-18
-9	0*	26
K= 6, L= 6		
0	133	-134
1	56	-71
2	46*	45
3	86	83
4	57	51
0	135	-134
-1	93	92
-2	58	45
-3	0*	3
-4	114	-110
-5	42*	32
-6	59	46
-7	64	50
K= -6, L= 6		
0	57	61
0	61	61
1	194	212
2	101	125
3	19*	-48
4	0*	14
5	54	-9
6	0*	21
-1	299	-350
-2	283	-329
-3	3*	-31
-4	103	114
-5	69	96
-6	97	-85
-7	108	-115
-8	162	-180
-9	65	-77
K= 7, L= 6		
0	142	-162
1	79	-29
2	62	72
3	83	98
0	151	-162
-1	51*	-71
-2	82	86
-3	139	155
-4	63	76
-5	65	-69
-6	35*	-24
K= -7, L= 6		
0	105	97
0	94	96
1	135	155
2	128	137
3	0*	17
4	55	-59
5	33*	13
6	0*	43
-1	34*	-1
-2	153	168
-3	193	233
-4	107	110
-5	44	-31
-6	31*	-9
-7	25*	-3
-8	85	84
-9	93	100
K= 8, L= 6		
0	45*	-11
1	77	66
2	92	103
0	0*	-11
-1	88	-79
-2	72	-35
-3	28*	43
-4	53*	39
-5	0*	-35
K= -8, L= 6		
0	263	-287
0	265	-287
1	51	-57
2	82	72
3	120	125
4	42*	-53
5	77	-79
6	72	-78
-1	235	-245
-2	77	86
-3	271	291
-4	153	159
-5	144	-142
-6	37*	-37
-7	80	49
-8	45*	55
K= 9, L= 6		
0	0*	13
0	32*	13
-1	33*	-39
-2	33*	-31
-3	61	45
K= -9, L= 6		
0	129	-143
0	126	-143
1	70	-74
2	0*	-1
3	0*	-39
4	0*	31
5	61	-39
-1	43	36
-2	44	29
-3	34*	-3
-4	147	-161
-5	80	-95
-6	70	-69
-7	40*	27
-8	44*	27
K= -10, L= 6		
0	0*	27
0	15*	27
1	24*	-38
2	53	19
3	92	86
4	81	81
K= -10, L= 6		
-1	31*	4
-2	24*	45
-3	43*	-8
-4	0*	-9
-5	29*	-5
-6	43*	2
-7	22*	-34
K= -11, L= 6		
0	141	138
0	137	138
1	0*	5
2	83	-68
3	69	-53
4	0*	-6
K= -11, L= 6		
-1	106	103
-2	37*	21
-3	54	-41
-4	72	-38
-5	37*	28
-6	85	91
K= -12, L= 6		
0	0*	25
0	10*	23
1	26*	16
2	45*	-45
K= -12, L= 6		
-1	0*	-29
-2	46*	-52
-3	44*	-34
-4	61	34
-5	65	62
K= -13, L= 6		
0	0*	-14
0	0*	-14
K= -13, L= 6		
-1	42*	25
-2	72	-40
K= 0, L= 7		
0	53	-55
1	145	234
2	97	97
3	110	-130
4	130	-163
5	121	-132
6	65	25
0	55	-56
-1	144	-233
-2	351	-313
-3	421	390
-4	130	150
-5	18*	-42
-6	180	-162
-7	201	202
-8	72	64
-9	115	116
-10	53*	-32
K= 1, L= 7		
0	162	174
1	257	304
2	11*	23
3	62	53
4	59	-50
5	20*	-3
6	26*	53
0	170	174
-1	53	-47
-2	230	-213
-3	155	-45
-4	365	344
-5	241	230
-6	133	108
-7	237	-233
-8	97	-94
-9	50*	-26
K= -1, L= 7		
0	443	-453
0	437	-453
1	100	85
2	237	249
3	57	47
4	51	-25
5	10*	2
6	73	-42
-1	507	-505
-2	55	42
-3	241	203
-4	135	120
-5	133	-145
-6	35*	-34
-7	123	-114
-8	56	-51
-9	24*	24
-10	63	47
K= 2, L= 7		
0	419	417
1	34*	4
2	206	-206
3	90	-105
4	21*	-13
5	101	115
6	76	43
0	403	417
-1	157	148
-2	109	-110
-3	446	-445
-4	57	-60
-5	70	75
-6	50	12
-7	50	35
-8	47*	-14
-9	0*	-31
K= -2, L= 7		
0	164	-145
0	178	-145
1	93	-95
2	144	140
3	128	133
4	20*	21
5	95	-96
6	13*	-12
-1	0*	21
-2	361	344
-3	77	81
-4	437	-437
-5	322	-341
-6	0*	-26
-7	0*	20
-8	66	50
-9	66	-61
-10	74	-76
K= 3, L= 7		
0	55	56
1	206	-221
2	67	-40
3	63	-42
4	49*	42
5	30*	22
0	59	54
-1	131	-69
-2	94	-74
-3	252	-262
-4	139	-95
-5	65	104
-6	45*	52
-7	59	-51
-8	63	-73
-9	57	-65
K= -3, L= 7		
0	113	-116
0	113	-116
1	336	-343
2	42	-44
3	142	147
4	191	197
5	65	44
6	49*	-71
-1	276	272
-2	573	587
-3	263	291
-4	147	-140
-5	69	56
-6	61	62
-7	77	74
-8	65	83
-9	23*	-26
-10	71	51
K= 4, L= 7		
0	81	79
1	269	-220
2	86	-89
3	34*	45
4	93	110
5	31*	-8
6	63	79
-1	433	474
-2	96	125
-3	82	-73
-4	156	-166
-5	51	56
-6	113	106
-7	79	63
-8	91	79
K= -4, L= 7		
0	261	291
0	261	291
1	198	-207
2	237	-250
3	102	-108
4	41*	27
5	36*	39
6	0*	-30
-1	156	165
-2	80	83
-3	379	-419
-4	69	-90
-5	14*	-19
-6	185	217
-7	192	236
-8	0*	-7
-9	57	76
-10	0*	-34
K= 5, L= 7		
0	223	-247
1	27*	-22
2	80	66
3	139	151
4	0*	23
0	221	-247
-1	0*	-40
-2	177	195
-3	85	85
-4	63	-72
-5	71	-87
-6	36*	52
-7	22*	-15
-8	61	-52
K= -5, L= 7		
0	270	-270
0	263	-270
1	41	-16
2	158	-169
3	23*	27
4	20*	15
5	75	73
6	42*	3
-1	207	230
-2	227	-203
-3	149	-213
-4	156	-186
-5	52	40
-6	84	-76
-7	207	-235
-8	101	-121
-9	42*	-35
K= 6, L= 7		
0	121	-152
1	41*	-43
2	52*	51
3	55*	45
0	137	-152
-1	42	-95
-2	125	136
-3	75	75
-4	56	-51
-5	115	-115
-6	72	-86
-7	0*	31
K= -6, L= 7		
0	447	451
0	447	451
1	292	320
2	44	47
3	153	-157
4	0*	-17
5	13*	34
6	53*	59
-1	0*	-3
-2	195	-220
-3	132	-130
-4	131	135
-5	219	234
-6	49	72
-7	57	-44
-8	15*	-13
-9	23*	-57
K= 7, L= 7		
0	23*	-54
1	27*	44
2	37*	49
0	40*	-54
-1	66	-68
-2	32*	10
-3	44	67
-4	30*	52
-5	0*	7
-6	0*	-4
K= -7, L= 7		
0	0*	-29
0	15*	-27
1	69	104
2	47	63
3	45*	-55
4	22*	-45
5	0*	-8
6	40*	29
-1	175	-189
-2	55	-49
-3	146	157
-4	255	289
-5	139	175
-6	43*	-49
-7	22*	-45
-8	0*	-2
-9	99	110
K= 8, L= 7		
0	9*	13
0	34*	13
-1	0*	-32
-2	43*	-53
-3	0*	9
-4	48*	36
K= -8, L= 7		
0	119	-134
0	117	-134
1	43*	35
2	114	128
3	81	-78
4	136	-108
5	62	-54
-1	174	-187
-2	39*	-47
-3	41*	-52
-4	53	-57
-5	180	-183
-6	82	93
-7	29*	24
-8	45*	51
K= -9, L= 7		
0	156	-159
0	159	-159
1	101	-109
2	107	104
3	92	86
4	0*	15
5	57	29
K= -9, L= 7		
-1	0*	34
-2	117	126
-3	144	166
-4	83	-95
-5	48	-40
-6	197	-222
-7	11*	-27
-8	0*	-10
K= -10, L= 7		
0	62	-52
0	64	-52
1	17*	-6
2	33*	-27
3	140	131
4	54*	-23
K= -10, L= 7		
-1	42*	41
-2	140	144
-3	0*	26
-4	0*	-26
-5	67	-66
-6	60	68
-7	100	36
K= -11, L= 7		
0	63	-48
0	47*	-48
1	86	-86
2	0*	-27
3	0*	-2
K= -11, L= 7		
-1	64	74
-2	48*	50
-3	57	32
-4	0*	-14
-5	0*	-34
-6	40*	45
K= -12, L= 7		
0	38*	35
0	54	35
1	35*	-12
2	20*	-6
K= -12, L= 7		
-1	61	3
-2	90	-60
-3	69	-64
-4	72	-52
-5	40*	-3
K= -13, L= 7		
0	43*	61
0	60	61
K= -13, L= 7		
-1	0*	4
-2	17*	9
-3	20*	-23
K= 0, L= 8		
0	73	46
1	76	69
2	28*	-5
3	73	-73
4	105	-116
5	0*	43
0	65	40
-1	220	-230
-2	92	-106
-3	28*	-13
-4	240	236
-5	45	-27
-6	120	-126
-7	0*	-25
-8	0*	14
-9	75	54
K= 1, L= 8		
0	315	328
1	56	60
2	0*	-8
3	154	-154
4	75	-86
5	36*	2
0	316	324
-1	37*	27
-2	236	-294
-3	234	-249
-4	56	49
-5	365	370
-6	65	73
-7	0*	-46
-8	63	23
-9	44*	3
K= -1, L= 8		
0	166	-165
0	167	-165
1	252	247
2	280	304
3	18*	1
4	144	-139
5	97	-102
6	65	73
-1	237	-245
-2	285	-276
-3	43	-18
-4	218	221
-5	54	42
-6	183	-168
-7	153	-163
-8	0*	-27
-9	58	-54
-10	25*	-41
K= 2, L= 8		
0	167	186
1	52	-23
2	102	-118
3	48	-93
4	132	154
5	73	93
0	169	186
-1	287	304
-2	32*	-25
-3	67	-69
-4	60	-58
-5	143	144
-6	58	70
-7	99	-113
-8	44*	-45
-9	38*	14
K= -2, L= 8		
0	238	-242
0	249	-242
1	55	-51
2	111	111
3	193	198
4	11*	25
5	65	-49
6	103	-72
-1	144	-149
-2	264	264
-3	447	455
-4	113	121
-5	160	-157
-6	206	-204
-7	0*	19
-8	56	52
-9	67	63
-10	0*	-5
K= 3, L= 8		
0	189	-193
1	52	32
2	123	-135
3	50*	31
4	0*	-9
0	192	-193
-1	195	213
-2	76	86
-3	169	-182
-4	235	-256
-5	123	-113
-6	106	118
-7	49*	57
-8	0*	-40
K= -3, L= 8		
0	87	-84
0	89	-84
1	64	-70
2	119	126
3	100	98
4	52	-27
5	101	-80
6	32*	-18
-1	37*	-35
-2	181	175
-3	74	81
-4	19*	-29
-5	32*	-25
-6	226	223
-7	210	225
-8	101	96
-9	18*	-35
-10	31*	-7
K= 4, L= 8		
0	0*	-11
1	177	-205
2	43*	-54
3	60*	71
4	33*	66
0	21*	-11
-1	89	-105
-2	167	197
-3	47*	51
-4	0*	18
-5	133	-143
-6	27*	-17
-7	77	62
-8	0*	-9
K= -4, L= 8		
0	143	-150
0	149	-150
1	312	-308
2	263	-264
3	0*	26
4	67	80
5	32*	45
6	43*	-28
-1	263	272
-2	123	152
-3	162	-151
-4	324	-344
-5	273	-293
-6	24*	-35
-7	4*	-15
-8	31*	-40
-9	24*	32
-10	31*	22
K= 5, L= 8		
0	0*	-23
1	65	-31
2	60	95
3	67	52
0	49*	-23
-1	36*	-34
-2	125	136
-3	162	176
-4	0*	-52
-5	45*	-47
-6	25*	23
-7	99	76
K= -5, L= 8		
0	154	166
0	156	166
1	135	-138
2	82	-76
3	55	40
4	143	144
5	48*	6
6	0*	-17
-1	415	438
-2	99	-100
-3	289	-311
-4	181	-203
-5	188	201
-6	98	111
-7	0*	5
-8	81	-83
-9	136	-172
K= 6, L= 8		
0	83	-92
1	0*	26
2	43*	70
0	93	-92
-1	98	-105
-2	17*	-51
-3	114	114
-4	25*	43
-5	4*	-62
-6	69	-97
K= -6, L= 8		
0	372	404
0	361	404
1	51	40
2	140	-150
3	118	-128
4	56	61
5	95	98
-1	75	78
-2	13*	16
-3	25*	-41
-4	127	132
-5	120	133
-6	49	46
-7	0*	36
-8	36*	43
-9	104	95
K= 7, L= 8		
0	15*	22
0	41*	22
-1	50*	-37
-2	100	-105
-3	0*	-19
-4	64	59
-5	51*	26
K= -7, L= 8		
0	86	101
0	84	101
1	65	62
2	53	-49
3	51	-29
4	64	-76
5	20*	-42
-1	193	-211
-2	254	-291
-3	136	-130
-4	178	198
-5	114	143
-6	11*	8
-7	85	-77
-8	31*	-33
-9	34*	35
K= -8, L= 8		
0	0*	-43
0	55	-43
1	142	150
2	11*	-17
3	35*	-42
4	50*	-43
5	47*	27
K= -8, L= 8		
-1	132	-103
-2	142	-149
-3	31*	26
-4	92	97
-5	75	-76
-6	85	-93
-7	131	-151
-8	28*	-6
K= -9, L= 8		
0	52	-63
0	72	-63
1	133	144
2	137	145
3	43*	18
4	14*	7
K= -9, L= 8		
-1	91	-105
-2	100	-112
-3	147	170
-4	95	99
-5	81	105
-6	126	-130
-7	0*	15
-8	33*	-52
K= -10, L= 8		
0	37*	-32
0	38*	-32
1	41*	-38
2	20*	7
3	31*	-39
4	43*	-5
K= -10, L= 8		
-1	33*	31
-2	199	199
-3	50	39
-4	38*	-50
-5	74	-74
-6	106	94
-7	19*	27
K= -11, L= 8		
0	82	-56
0	61	-56
1	116	-106
2	29*	43
3	30*	34
K= -11, L= 8		
-1	59	-26
-2	33*	36
-3	52	-20
-4	42*	-44
-5	38*	-5
K= -12, L= 8		
0	0*	-1
1	58	-29
K= 0, L= 9		
0	111	113
1	173	180
2	0*	9
3	117	-117
4	23*	-22
5	0*	41
0	106	113
-1	94	-78
-2	302	-311
-3	145	-151
-4	156	105
-5	103	116
-6	163	171
-7	167	-176
-8	114	-118
-9	63	-56
K= 1, L= 9		
0	175	181
1	30*	-1
2	232	-249
3	115	-110
4	47*	-1
0	173	181
-1	151	150
-2	12*	-30
-3	189	-196
-4	47	-66
-5	28*	-10
-6	81	88
-7	58	53
-8	24*	-4
-9	90	72
K= -1, L= 9		
0	116	114
0	105	114
1	178	188
2	81	95
3	114	-116
4	78	-87
5	0*	5
-1	71	-75
-2	256	-248
-3	96	83
-4	82	72
-5	76	47
-6	304	-296
-7	43*	-43
-8	53*	61
-9	27*	52
K= 2, L= 9		
0	212	227
2	80	-93
4	100	110
0	202	227
-1	0*	-26
-2	68	75
-3	87	-98
-4	0*	-12
-5	0*	41
-6	98	107
-7	65	67
-8	64	-62
-9	70	-76
K= -2, L= 9		
0	200	-213
0	205	-213
1	196	192
2	108	117
3	118	129
4	46*	-67
5	0*	-18
-1	295	-311
-2	202	176
-3	339	353
-4	275	280
-5	27*	-37
-6	0*	6
-7	34*	26
-8	65	47
-9	59	31
K= 3, L= 9		
0	102	-92
1	143	-151
2	18*	-54
3	71	97
0	83	-92
-1	237	263
-2	144	150
-3	57	60
-4	192	-204
-5	73	-59
-6	0*	-26
-7	93	80
-8	23*	47
K= -3, L= 9		
0	314	-315
0	312	-315
1	126	-121
2	184	198
3	0*	-6
4	48*	-69
5	126	-138
-1	172	-171
-2	126	133
-3	295	297
-4	124	-99
-5	282	-284
-6	89	-99
-7	78	77
-8	126	125
-9	71	49
K= 4, L= 9		
0	102	-114
1	85	-89
2	43*	37
3	61	62
0	102	-114
-1	72	-83
-2	29*	-19
-3	75	87
-4	0*	-6
-5	96	-112
-6	43*	-41
-7	58	31
K= -4, L= 9		
0	253	-243
0	251	-243
1	192	-208
2	102	113
3	144	153
4	65	62
5	0*	0
-1	130	-137
-2	201	205
-3	109	107
-4	188	-187
-5	164	-186
-6	93	-98
-7	47	-43
-8	82	-81
-9	70	-76
K= 5, L= 9		
0	46*	-54

Table 4 (*cont.*)

H	FO	FC
K= 5, L= 9		
1	42*	12
2	2*	32
3	44*	-34
-1	0*	-6
-2	0*	16
-3	67	90
-4	64	70
-5	38*	-30
-6	37*	-44
K= -5, L= 9		
0	173	175
0	167	175
1	45	-20
2	71	-79
3	24*	33
4	17*	32
5	75	47
-1	290	244
-2	320	352
-3	160	-186
-4	118	-124
-5	24*	-27
-6	173	172
-7	174	157
-8	0*	20
-9	44*	-43
K= 6, L= 9		
0	3*	-16
0	0*	-16
-1	48*	-77
-2	66	-20
-3	29*	-12
-4	110	104
-5	34*	36
K= -6, L= 9		
0	135	-151
0	140	-151
1	45	49
2	145	-142
3	40*	-16
4	14*	4
5	32*	32
-1	168	175
-2	36*	-40
-3	60*	-37
-4	67	-65
-5	165	137
-6	164	184
-7	22*	-15
-8	44*	-41
-9	51*	13
K= 7, L= 9		
0	260	273
0	258	273
1	111	-115
2	55	-73
3	139	-124
4	35*	25
5	0*	-6
K= -7, L= 9		
-1	111	120
-2	233	-264
-3	274	-305
-4	96	-137
-5	23*	52
-6	3*	43
-7	0*	-7
-8	0*	3
-9	45*	-33
K= 8, L= 9		
0	75	86
0	73	86
1	40*	52
2	52	40
3	41*	75
4	30*	1
K= -8, L= 9		
-1	67	-62
-2	91	-101
-3	66	48
-4	144	153
-5	46*	58
-6	164	-137
-7	124	-117
-8	62	-62
K= 9, L= 9		
0	39*	59
0	45*	59
1	95	101
2	0*	16
3	33*	-8
4	55*	-48
K= -9, L= 9		
-1	111	-108
-2	13*	-16
-3	110	102
-4	151	106
-5	0*	2
-6	42*	-50
-7	86	87
-8	41*	58
K= -10, L= 9		
0	133	-113
0	113	-113
1	0*	4
2	37*	3
3	42*	20
K= -10, L= 9		
-1	105	-105
-2	17*	-3
-3	96	84
-4	71	82
-5	0*	-15
-6	51	-11
-7	0*	-50
K= -11, L= 9		
0	0*	-16
0	3*	-15
1	0*	4
2	24*	15
K= -11, L= 9		
-1	57	-46
-2	0*	-20
-3	24*	23
-4	84	-84
-5	131	-121
-6	42*	-32
K= -12, L= 9		
0	57	-17
0	0*	-17
1	0*	-14
K= -12, L= 9		
-1	45*	43
-2	74	61
-3	26*	55
-4	0*	-26
-5	0*	1
K= 0, L= 10		
0	206	221
1	82	103
2	82	-80
3	97	-104
4	0*	-9
0	199	221
-1	124	143
-2	232	-230
-3	222	-236
-4	74	-68
-5	138	143
-6	65	68
-7	74	-91
-8	85	-71
-9	69	-60
K= 1, L= 10		
0	64	71
1	140	-157
2	140	-153
3	0*	37
0	70	71
-1	192	214
-2	51	-7
-3	145	-145
-4	103	-102
-5	11*	47
-6	76	81
-7	14*	-23
-8	26*	-33
-9	30*	-6
K= -1, L= 10		
0	168	173
0	170	173
1	112	126
2	15*	-27
3	76	-96
4	0*	-13
-1	61	-64
-2	207	-207
-3	28*	39
-4	221	233
-5	242	263
-6	170	-148
-7	25*	-4
-8	63	-66
-9	49*	64
K= 2, L= 10		
0	0*	-26
1	86	-98
2	51*	-59
3	0*	-2
0	0*	-26
-1	0*	47
-2	147	160
-3	34*	-43
-4	137	-142
-5	73	-78
-6	89	83
-7	100	86
-8	0*	29
K= -2, L= 10		
0	107	105
0	109	105
1	213	201
2	60	60
3	86	-76
4	101	-104
-1	172	-169
-2	123	-124
-3	193	-195
-4	203	195
-5	136	117
-6	154	163
-7	67	-66
-8	63	56
-9	40*	42
K= 3, L= 10		
0	98	-115
1	102	-111
2	45*	46
0	117	-115
-1	109	119
-2	131	139
-3	66	67
-4	26*	9
-5	29*	-15
-6	60*	-32
-7	50*	-9
K= -3, L= 10		
0	176	-180
0	172	-180
1	82	-103
2	89	92
3	50*	62
4	15*	-14
-1	193	-193
-2	58	-45
-3	182	186
-4	72	86
-5	244	-233
-6	280	-305
-7	98	-112
-8	26*	25
-9	17*	22
K= 4, L= 10		
0	116	-111
1	[illegible]	-1
0	112	-111
-1	29*	-40
-2	64	75
-3	0*	16
-4	0*	-11
-5	45*	-7
K= -4, L= 10		
0	126	-124
0	130	-124
1	17*	30
2	93	91
3	109	111
4	49*	-1
-1	34*	40
-2	137	134
-3	197	205
-4	32*	-16
-5	157	-147
-6	0*	0
-7	112	113
-8	77	64
-9	84	-77
K= 5, L= 10		
0	66	-70
0	0*	-70
-1	140	-151
-2	59	-10
-3	54*	49
-4	61	40
-5	56*	31
K= -5, L= 10		
0	165	-177
0	172	-177
2	0*	-10
3	75	77
4	66	62
-1	95	99
-2	267	286
-3	241	246
-4	31*	-107
-5	92	-113
-6	47*	36
-7	131	139
-8	0*	39
-9	31*	70
K= 6, L= 10		
-3	23*	65
K= -6, L= 10		
0	75	-74
0	76	-74
1	83	-84
2	32*	-31
3	0*	-13
4	67*	0
-1	0*	26
-2	67	52
-3	42	-97
-4	293	-319
-5	38*	19
-6	104	104
-7	58	53
-8	28*	-6
-9	53*	-59
K= -7, L= 10		
0	213	232
0	215	232
1	55	-58
2	75	-85
3	56	-96
4	75	84
K= -7, L= 10		
-1	29*	-16
-2	42	94
-3	211	-221
-4	27*	17
-5	0*	-31
-6	12*	30
-7	40	-63
-8	129	-126
-9	3*	-17
K= -8, L= 10		
0	14*	-21
0	42*	-21
1	176	178
2	0*	8
3	3*	-7
4	35*	-58
K= -8, L= 10		
-1	112	123
-2	113	-119
-3	91	-102
-4	47	41
-5	151	162
-6	130	151
-7	3*	-26
-8	45*	-57
K= -9, L= 10		
0	26*	21
0	45*	21
1	3*	-1
2	3*	-4
3	53*	-70
K= -9, L= 10		
-1	15*	31
-2	27*	-56
-3	40*	29
-4	3*	18
-5	59	65
-6	0*	3
-7	6*	-19
-8	94	80
K= -10, L= 10		
0	5*	-12
0	32*	-12
1	3*	-9
2	66	48
K= -10, L= 10		
-1	104	-96
-2	68	-79
-3	0*	-17
-4	33*	10
-5	63	63
-6	105	-107
-7	28*	-38
K= -11, L= 10		
0	3*	-30
0	30*	-30
1	0*	-14
K= -11, L= 10		
-1	3*	-30
-2	101	90
-3	13*	34
-4	50*	27
-5	144	-147
-6	0*	-17
K= -12, L= 10		
0	44*	-22
0	57	-22
K= -12, L= 10		
-1	49*	39
-2	15*	9
-3	19*	49
-4	56*	6
K= 0, L= 11		
0	64	62
1	78	-47
2	109	-115
3	26*	-22
0	61	62
-1	138	154
-2	102	94
-3	111	-110
-4	105	-107
-5	60	-49
-6	68	41
-7	34*	50
-8	49*	-34
K= 1, L= 11		
0	99	101
1	125	-140
2	67	-47
0	86	101
-1	41	98
-2	42*	37
-3	91	-83
-4	117	-111
-5	34*	-8
-6	74	60
-7	61	61
-8	53*	-43
K= -1, L= 11		
0	135	133
0	137	133
1	113	114
2	47*	-52
3	88	-84
-1	3*	20
-2	79	-101
-3	136	-113
-4	112	103
-5	114	113
-6	173	187
-7	23*	0
-8	20*	-36
-9	35*	-1
K= 2, L= 11		
0	169	-183
1	81	-84
2	36*	-2
0	171	-183
-1	79	71
-2	159	181
-3	87	96
-4	155	-150
-5	105	-159
-6	54*	-5
-7	50*	42
K= -2, L= 11		
0	63	58
0	61*	58
1	99	103
2	74	-21
3	113	-112
-1	64*	-63
-2	236	-245
-3	47	-64
-4	74	54
-5	127	137
-6	85	-75
-7	248	-250
-8	48*	29
-9	42*	66
K= 3, L= 11		
0	69	-97
1	42*	3
0	97	-97
-1	70	-89
-2	44*	46
-3	70	64
-4	0*	26
-5	75	-38
-6	42*	-31
-7	61	63
K= -3, L= 11		
0	27*	12
0	20*	12
1	114	122
2	120	113
3	26*	29
4	58	-63
-1	262	-245
-2	202	-204
-3	121	121
-4	131	140
-5	103	125
-7	25*	-55
-8	69	-79
-9	0*	-28
K= 4, L= 11		
0	48*	-35
0	39*	-35
-1	70	-62
-2	37*	12
-3	115	121
-4	44*	59
-5	31*	-15
K= -4, L= 11		
0	43*	-18
0	35*	-18
1	52	42
2	87	103
3	33*	-3
4	0*	-48
-1	3*	-3
-2	136	125
-3	69	63
-4	153	162
-5	3*	5
-6	95	-87
-8	113	97
-9	83	98
K= -5, L= 11		
0	195	-198
0	191	-198
1	113	-121
2	3*	4
3	95	104
4	32*	14
K= -5, L= 11		
-1	37*	-22
-2	79	83
-3	36*	17
-4	62	61
-5	107	-90
-6	0*	-15
-7	42*	18
-8	11*	32
-9	3*	14
K= -6, L= 11		
0	42*	-27
0	27*	-27
1	141	-142
2	55	-60
3	0*	25
K= -6, L= 11		
-1	151	161
-2	86	73
-3	35*	-26
-4	199	-210
-5	175	-184
-6	38*	-16
-7	63	57
-8	84	132
-9	64	-86
K= -7, L= 11		
0	73	92
0	77	92
1	0*	-19
2	3*	-22
3	21*	27
K= -7, L= 11		
-1	29*	18
-2	3*	30
-3	91	34
-4	35*	-14
-5	13*	-17
-6	23*	41
-7	3*	21
-8	78	-88
K= -8, L= 11		
0	62	58
0	64	58
1	0*	-7
2	71	-58
3	17*	-33
K= -8, L= 11		
-1	133	139
-2	22*	-7
-3	36*	-69
-4	18*	-69
-5	89	84
-6	94	60
-7	42*	68
-8	0*	34
K= -9, L= 11		
0	43*	26
0	71	26
1	73	62
2	26*	-15
K= -9, L= 11		
-1	112	-115
-2	115	-116
-3	54	-44
-4	43	47
-5	44	77
-6	17*	5
-7	72	-63
K= -10, L= 11		
0	57	42
0	40*	42
1	20*	52
2	0*	12
K= -10, L= 11		
-1	33*	-43
-2	66	-71
-3	50	-31
-4	0*	3
-5	14*	-14
-6	95	-83
-7	30*	-36
K= -11, L= 11		
0	3*	-22
0	0*	-22
1	44*	17
K= -11, L= 11		
-1	42*	-24
-2	0*	-7
-3	67	63
-4	101	40
-5	35*	-14
-6	13*	52
K= -12, L= 11		
-1	0*	2
-2	47*	-14
-3	24*	44
-4	0*	-1
K= 0, L= 12		
0	41	-82
1	92	-86
2	54*	-52
0	74	-82
-1	194	213
-2	64	71
-3	0*	-8
-4	66	-45
-5	61	37
-6	64	63
-7	30*	55
-8	63*	4
K= 1, L= 12		
0	34*	28
1	44	-45
0	0*	28
-1	29*	-4
-2	44	134
-3	0*	-16
-4	38*	-34
-5	127	-130
-6	36*	5
-7	51*	35
K= -1, L= 12		
0	148	160
0	158	160
1	34*	-13
2	46	-54
-1	116	167
-2	46*	-65
-3	128	-151
-4	128	-139
-5	76	67
-6	83	90
-7	111	107
-8	0*	-10
K= 2, L= 12		
0	114	-133
0	111	-133
-1	25*	-24
-2	63	76
-3	82	84
-4	0*	-4
-5	41*	-17
-6	0*	-31
K= -2, L= 12		
0	83	105
0	108	105
1	30*	32
2	92	-74
-1	44*	-69
-2	102	-109
-3	82	-87
-4	0*	25
-5	43*	31
-6	112	-105
-7	54	-25
-8	122	-121
K= 3, L= 12		
-1	44*	-84
-2	42*	13
-3	31*	62
-4	54	34
-5	31*	-43
K= -3, L= 12		
0	89	82
0	97	82
1	173	176
2	40*	25
3	44*	-52
-1	72	-86
-2	0*	-14
-3	11*	33
-4	130	140
-5	85	-64
-6	172	173
-7	0*	-15
-8	0*	-12
K= 4, L= 12		
0	91	-123
0	133	-123
1	45*	37
2	131	145
3	72	-36
K= -4, L= 12		
-1	131	-138
-2	101	-107
-3	219	217
-4	145	148
-5	87	78
-6	97	-94
-7	116	-111
-8	74	61
K= -5, L= 12		
0	83	-92
0	95	-92
1	41*	15
2	16*	29
3	41*	34
K= -5, L= 12		
-1	128	-122
-2	31*	25
-3	0*	36
-4	102	-53
-5	44*	-46
-6	85	-91
-7	52	19
-8	0*	31
K= -6, L= 12		
0	82	-79
0	60	-79
1	81	-66
2	41*	40
3	81	66
K= -6, L= 12		
-1	0*	20
-2	163	175
-3	32*	61
-4	33*	-13
-5	77	-75
-6	55	-62
-7	0*	-9
-8	54	-44
K= -7, L= 12		
0	47*	-14
0	2*	-14
1	24*	-39
2	31*	-22
K= -7, L= 12		
-1	125	128
-2	78	69
-3	36*	-37
-4	76	-84
-5	16*	0
-6	127	135
-7	23*	77
-8	20*	21
K= -8, L= 12		
0	37*	50
0	11*	50
1	129	-123
2	62	-64
K= -8, L= 12		
-1	115	111
-2	41*	27
-3	96	-100
-4	64	-51
-5	0*	17
-6	0*	40
-7	33*	38
-8	39*	27
K= -9, L= 12		
0	53*	17
0	34*	14
1	87	76
K= -9, L= 12		
-1	56	-12
-2	64	-66
-3	76	-73
-4	63	-55
-5	0*	11
-6	0*	9
-7	44*	-25
K= -10, L= 12		
0	63	46
0	57	46
1	32*	5
K= -10, L= 12		
-1	34*	-8
-2	22*	-10
-3	49*	8
-4	73	55
-5	26*	21
-6	40*	-14
K= -11, L= 12		
-1	0*	-15
-2	44*	-43
-3	37*	16
-4	79	57
-5	81	57
K= 0, L= 13		
0	62	-74
0	52*	-74
-1	144	151
-2	77	65
-3	56	-41
-4	57	-69
-5	31*	26
-6	70	45
-7	34*	40
K= 1, L= 13		
0	90	-116
0	93	-116
-1	3*	-52
-2	111	130
-3	40	102
-4	0*	-22
-5	87	-90
-6	42*	-33
K= -1, L= 13		
0	27*	18
0	0*	18
1	65	-73
-1	49*	49
-2	50*	46
-3	96	-91
-4	68	-65
-5	24*	-27
-6	0*	-6
-7	43*	-70
K= 2, L= 13		
-2	3*	10
-3	66	73
-4	0*	3
-5	41*	-11
K= -2, L= 13		
0	104	126
0	111	126
1	0*	8
-1	73	81
-2	77	-82
-3	147	-143
-4	0*	-11
-5	121	120
-6	59	73
-7	18*	4
-8	32*	-24
K= -3, L= 13		
0	105	110
0	99	110
1	43*	53
2	32*	-34
K= -3, L= 13		
-1	54	47
-2	54	-71
-3	78	-63
-4	66	53
-5	93	88
-6	61	73
-7	50*	-63
-8	75	20
K= -4, L= 13		
0	53	20
0	3*	20
1	76	63
2	23*	30
K= -4, L= 13		
-1	115	-133
-2	185	-188
-3	51	44
-4	105	94
-5	76	57
-6	155	-153
-7	73	50
-8	55*	-60
K= -5, L= 13		
0	61	-59
0	54	-59
1	63	92
2	23*	4
K= -5, L= 13		
-1	108	-99
-2	69	55
-3	71	72
-4	75	66
-5	144	-127
-6	34*	-19
-7	52*	-47
-8	27*	17
K= -6, L= 13		
0	92	-87
0	75	-87
1	0*	3
2	105	105
K= -6, L= 13		
-1	82	-53
-2	67	43
-3	140	144
-4	3*	42
-5	43*	-41
-6	0*	-17
-7	53*	-3
-8	27*	23
K= -7, L= 13		
0	3*	-41
0	46*	-41
1	101	-86
K= -7, L= 13		
-1	48*	49
-2	116	102
-3	46*	55
-4	71	-67
-5	65	-40
-6	62	-13
-7	71	53
K= -8, L= 13		
0	45*	17
0	27*	17
1	55*	-62
K= -8, L= 13		
-1	3*	11
-2	12*	18
-3	102	-99
-4	32*	-15
-5	3*	-13
-6	51*	42
-7	25*	25
K= -9, L= 13		
0	56	-25
0	3*	-25
K= -9, L= 13		
-1	109	111
-2	26*	-3
-3	25*	-27
-4	126	-128
-5	0*	3
-6	0*	24
K= -10, L= 13		
-1	38*	-14
-2	0*	-10
-3	22*	-31
-4	72	48
-5	105	96
K= -11, L= 13		
-3	55*	-11
K= 0, L= 14		
-2	23*	66
-3	46*	27
-4	50*	-53
-5	68	-81
K= -1, L= 14		
-1	0*	28
-2	95	122
-3	44*	5
-4	103	-114
-5	56	-57
-6	36*	14
K= -2, L= 14		
0	92	65
0	92	65
K= -2, L= 14		
-1	144	135
-2	72	49
-3	74	-76
-4	60	-57
-5	0*	42
-6	99	95
-7	46*	31
K= -3, L= 14		
0	46*	35
0	6*	35
K= -3, L= 14		
-1	0*	32
-2	92	-99
-3	50*	-87
-4	0*	24
-5	108	114
-6	43*	38
-7	93	-91
K= -4, L= 14		
0	65	75
0	48*	75
K= -4, L= 14		
-1	33*	-26
-2	110	-116
-3	53	-55
-4	5*	21
-5	44*	22
-6	22*	-39
-7	17*	17
K= -5, L= 14		
0	37*	4
0	0*	9
K= -5, L= 14		
-1	81	-64
-2	47*	-43
-3	38*	19
-4	130	121
-5	55	61
-6	0*	-19
-7	133	-129
K= -6, L= 14		
0	0*	-10
0	0*	-10
K= -6, L= 14		
-1	85	-79
-2	43*	-1
-3	122	103
-4	60	56
-5	38*	-34
-6	0*	-61
-7	38*	53
K= -7, L= 14		
0	77	-73
0	76	-73
K= -7, L= 14		
-1	55*	-52
-2	27*	44
-3	64	73
-4	3*	7
-5	0*	-56
-6	46*	-56
-7	49*	24
K= -8, L= 14		
0	52*	-43
0	60	-43
K= -8, L= 14		
-1	16*	50
-2	82	48
-3	3*	-22
-4	82	-59
-5	71	-77
-6	37*	-24
K= -9, L= 14		
-1	95	96
-2	15*	61
-3	23*	7
-4	51*	-27
-5	43*	26
K= -10, L= 14		
-3	56*	-58
K= -2, L= 15		
-1	2*	-12
-1	31*	-12
-4	57*	-56
-4	3*	-56
K= -3, L= 15		
-2	3*	5
-2	49*	5
-3	112	-97
-3	81	-97
-4	95	-90
-4	105	-90
-5	3*	0
K= -4, L= 15		
-2	2*	-6
-2	1*	-6
-3	67	-62
-3	55*	-62
-4	0*	9
-4	3*	9
-5	49*	27
-5	3*	27
-6	43*	59
-6	56*	59
K= -5, L= 15		
-1	3*	-15
-1	45*	-15
-2	97	-103
-2	98	-103
-3	42*	-37
-3	41*	-37
-4	32*	62
-4	65	62
-5	131	129
-5	131	129
-6	3*	-35
-6	33*	-35
K= -6, L= 15		
-1	64	-65
-1	48*	-65
-2	73	-14
-2	48*	-14
-3	59	55
-3	31*	55
-4	76	58
-4	14*	58
-5	51*	-47
-5	3*	-47
-6	3*	-25
-6	57	-25
K= -7, L= 15		
-2	37*	-97
-2	18*	-97
-3	74	55
-3	66	55
-4	38*	30
-5	37*	-33
-5	37*	-33
K= -8, L= 15		
-3	73	60
-3	44*	60
-4	66	-37
-4	51*	-37

n Table 2, and for the hydrogen atoms in Table 3. The observed and calculated structure factors are given in Table 4. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Discussion

The principal objective of this study was to determine the molecular structure of an adduct for which the available chemical data were equivocal. This objective was achieved, and the structure determination proved particularly worthwhile in that the result was different from that tentatively proposed at the outset, although fully consistent with chemical analyses carried out during and subsequent to the X-ray analysis (Baldwin & Duncan, 1971*a*,*b*).

The molecular packing is illustrated in Fig. 2 and the closer intermolecular contacts are listed in Table 5. The closest contact involving the dithiocarboxylate group is S(1)–C(12) (3·67 Å). This interaction might be weakly ionic, although there is clearly no direct ionic interaction between N(1) and the negatively charged group. Apart from an interaction with C(17) (3·78 Å) the closest approach of the bromine atom is 3·96 Å, being across a center of inversion to a symmetry-related atom. As is apparent in Fig. 2, the centrosymmetrically-related isoquinolinium rings overlap somewhat, and there are many mutual contacts ranging

Table 5. *Intermolecular contacts*

All intermolecular contacts less than 3·75 Å are included. Roman numerals indicate molecules at the following symmetry-related positions:

I: $(1-x,1-y,1-z)$; II: $(1-x,1-y,2-z)$; III: $(\bar{x},1-y,1-z)$.

NBID–NBID		
S(1)—C(12)	III	3·78 Å
S(1)—C(6)	III	3·48
N(1)—C(15)	II	3·48
N(1)—C(16)	II	3·41
C(9)—C(16)	II	3·65
C(9)—C(17)	II	3·54
C(8)—C(16)	II	3·46
C(12)-C(15)	II	3·32
C(12)-C(14)	II	3·55
C(12)-C(16)	II	3·66
C(11)-C(16)	II	3·69
C(11)-C(11)	II	3·52
C(11)-C(10)	II	3·61
C(11)-C(14)	II	3·75
C(11)-C(17)	II	3·58
C(10)-C(17)	II	3·38
C(3)—C(7)	I	3·44

DMF–NBID	
O(1)—N(1)	3·64 Å
O(1)—C(8)	3·20
C(20)-C(15)	3·75
C(20)-C(2)	3·66
N(2)—C(2)	3·57
O(1)—C(3)	3·37
C(18)-C(5)	3·51
C(18)-C(6)	3·69
N(2)—C(6)	3·67

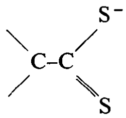
upwards from 3·4 Å in this region of the molecule (Table 5). The close approaches involving the dimethylformamide molecule of crystallization are also listed in Table 5. The oxygen atom approaches within 3·25 Å of C(7), and within 3·20 Å of C(8), these being the two closest approaches noted for the whole structure.

The non-hydrogen bond lengths and angles for NBID and in the dimethylformamide molecule are illustrated in Fig. 3. Standard deviations in the bond lengths range from 0·011 to 0·018 Å except for the C–S and C–Br bonds which are 0·010 and 0·008 Å. For the angles, the standard deviations range from 0·6 to 1·0° except in the dimethylformamide molecule, where they range from 1·1 to 1·3°. The bond lengths involving hydrogen atoms are listed in Table 6.

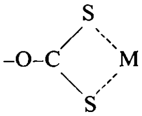
Table 6. *Bond lengths involving hydrogen atoms*

C(2)—H(2)	0·88 (12) Å	C(16)-H(16)	0·85 (13) Å
C(3)—H(3)	1·08 (12)	C(17)-H(17)	0·90 (13)
C(5)—H(5)	0·99 (12)		
C(6)—H(6)	1·01 (12)	C(18)-H(18)	0·70 (12)
C(7)—H(71)	0·88 (11)	C(19)-H(191)	1·01 (15)
C(7)—H(72)	0·88 (12)	C(19)-H(192)	1·08 (16)
C(8)—H(8)	1·04 (11)	C(19)-H(193)	1·11 (16)
C(12)-H(12)	0·84 (12)	C(20)-H(201)	1·05 (16)
C(14)-H(14)	0·89 (11)	C(20)-H(202)	1·12 (17)
C(15)-H(15)	1·17 (11)	C(20)-H(203)	0·66 (17)

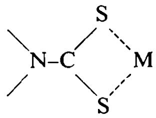
None of the interatomic distances appears to depart significantly from expected values (*International Tables for X-ray Crystallography*, 1962, Vol. III, p. 275). One of the more interesting features of the structure determination is the dithiocarboxylate group (III) for which we have not been able to find a strictly comparable example in the crystallographic literature. The observed C–S bond lengths in NBID, 1·693 (10) and 1·649 (10) Å, are probably not significantly different, and have an average value of 1·671 Å which, according to the carbon–sulphur bond length *vs* bond order plot of Abrahams (1956), corresponds to a double-bond character of 70%.



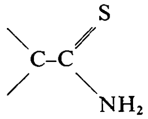
(III)



(IV)



(V)



(VI)

A comparison can be made between this carbon–sulphur bond length and those observed in a number of crystal structures in which the xanthate group is complexed to a variety of metals, as indicated by (IV). In cadmium ethylxanthate (Iimura, Ito & Hagihara, 1972) two xanthate groups complex the cadmium in a distorted tetrahedral arrangement, and the four independent C–S bonds are all essentially equal, ranging from 1·685 to 1·691 Å. In cobalt(III) ethylxanthate (Merlino, 1969) there is approximate octahedral coordination with the C–S bond lengths observed to be 1·674 and 1·671 Å, essentially similar to those in the cadmium complex and in NBID. In other xanthate complexes, *e.g.*, with lead (Hagihara, Watanabe & Yamashita, 1968), the metal–sulphur distances are significantly different, as are the carbon–sulphur bonds, so that a direct comparison with NBID cannot be made.

One may also compare the C–S bond lengths with those observed in dithiocarbamates (V). For example in the square planar nickel complex of diethyldithiocarbamate (Bonamico, Dessy, Mariani, Vaciago & Zambonelli, 1965) the two C–S bonds are 1·700 and 1·713 Å, and in hydrazinium hydrazinedithiocarboxylate, (Braibanti, Manotti Lanfredi, Tiripicchio & Logiudice, 1969) in which the dithiocarbamate anion participates in hydrogen bonding, rather than metal chelation, the C–S bond lengths are 1·695 and 1·723 Å, indicating slightly less double-bond character than for the dithiocarboxylate group in NBID.

On the other hand the C–S bond in the thioamido group (VI) of 2-thiamidopyridine and in 4-thiamidopyridine (Downie, Harrison, Raper & Hepworth, 1972) are both shorter (1·657 and 1·65 Å), reflecting higher double-bond character.

The equation of the best-fit least-squares plane through the isoquinolinium nucleus is

$$-0{\cdot}0060X+0{\cdot}7287Y-0{\cdot}6848Z=-5{\cdot}311\ \text{Å}$$

while that through the four atoms of the dithiocarboxylate side chain is

$$0{\cdot}1268X-0{\cdot}4127Y-0{\cdot}9020Z=-7{\cdot}300\ \text{Å}.$$

The equations of these planes are given for coordinates measured in Å relative to an orthogonal coordinate frame with the *X* axis parallel to **a**, and the *Z* axis parallel to **c***.

A χ^2 test shows that the isoquinolinium ring system is significantly non-planar. The departures from planarity, which are relatively small (Table 7), and presumably due to crystal packing forces, appear to be due primarily to the formation of a shallow dihedral angle between the two rings, along the line joining C(10) and C(11). The dithiocarboxylate side chain is planar within experimental error, and makes an angle of 71·6° with the isoquinolinium plane. Takano, Sasada & Kakudo (1966) have suggested that non-coplanarity is due to steric hindrance between side-chain atoms, and ring atoms *ortho* to the side chain, and that it is the van der Waals approach distance which defines the non-planarity angle. As the dithiocarboxylate group in NBID tends toward a coplanar configuration, impossibly short non-bonded interactions occur between one of the sulphur atoms and C(14). However it is not these contacts which are the closest ones in the crystal structure. Rather, the closest non-bonded approaches made by the sulphur atoms [excluding C(9)] are S(1)–C(10) (3·380 Å) and S(2)–C(8) (3·273 Å). The distances from C(14) are 3·449 Å for S(1) and 3·695 Å for S(2), and from H(14) are 2·86 Å for S(1) and 3·77 Å for S(2). The expected carbon–sulphur van der Waals distance is 3·35 Å (C = 1·50; S = 1·85 Å), although shorter approaches (2·96 and 3·15 Å) have been observed in 4- and 2-thioamidopyridine (Colleter & Gadret, 1967; Downie *et al.*, 1972).

Table 7. *Deviations from planarity*

Isoquinolinium nucleus	
N(1)	−0·011 (7) Å
C(8)	−0·027 (8)
C(9)	0·006 (8)
C(10)	0·032 (8)
C(11)	0·033 (8)
C(12)	0·008 (10)
C(14)	0·004 (10)
C(15)	−0·031 (10)
C(16)	−0·040 (11)
C(17)	0·000 (10)
C(7)*	−0·062 (10)
C(13)*	−0·024 (9)

Dithiocarboxylate group	
C(9)	−0·001 (13)
C(13)	0·004 (8)
S(1)	0·000 (3)
S(2)	0·000 (3)

Bromobenzyl ring	
C(1)	0·009 (10) Å
C(2)	−0·003 (11)
C(3)	−0·006 (11)
C(4)	0·005 (9)
C(5)	0·002 (11)
C(6)	−0·011 (11)
C(7)*	0·083 (10)
Br*	0·042 (1)

Dimethylformamide	
O(1)	0·007 (14)
N(2)	0·008 (10)
C(18)	−0·020 (14)
C(19)	0·010 (20)
C(20)	−0·015 (19)

* These atoms were not included in the calculation of the best-fit plane.

The best-fit least-squares plane through the bromobenzyl ring is

$$0{\cdot}7890X - 0{\cdot}5898Y - 0{\cdot}1723Z = 0{\cdot}207\ \text{Å}$$

and through the dimethylformamide molecule

$$-0{\cdot}9200X + 0{\cdot}3911Y - 0{\cdot}0235Z = 2{\cdot}697\ \text{Å}.$$

In neither case is there significant departure from planarity (Table 7). These two planes are only 17·3° from parallel, and as may be visualized in Fig. 2, the dimethylformamide molecules are interleaved between successive bromobenzyl rings related by translation along the *a* axis. The dihedral angle between the bromobenzyl and the isoquinolinium planes is 108·5°.

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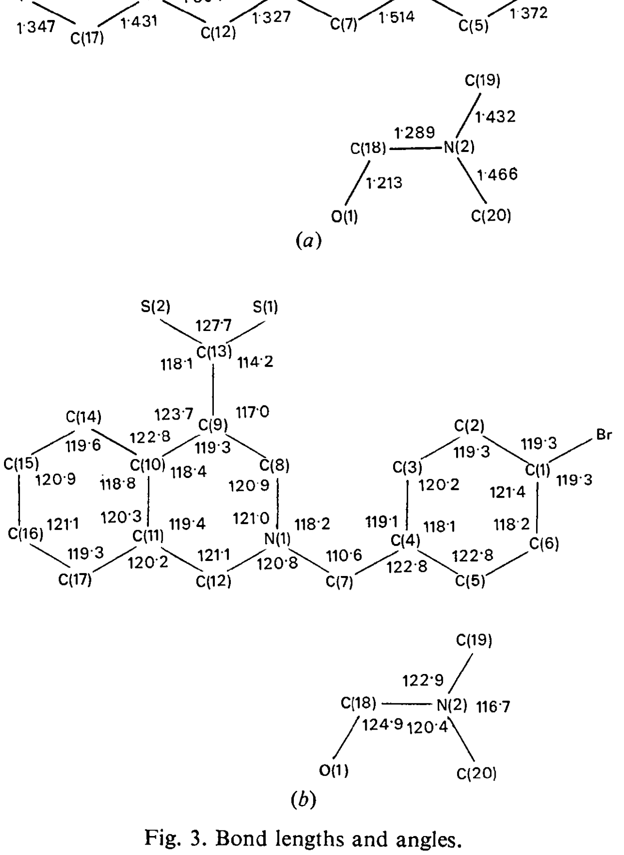

Fig. 3. Bond lengths and angles.

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The Crystal and Molecular Structure of Bacogenin-A$_1$ Dibromoacetate

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The crystal structure of bacogenin-A$_1$ dibromoacetate, $C_{34}H_{50}O_6Br_2$, has been determined in order to elucidate the molecular structure and absolute configuration of bacogenin-A$_1$, $C_{30}H_{48}O_4$, a triterpenoid sapogenin isolated from *Bacopa monniera*. The crystals are orthorhombic with space group $P2_12_12_1$ and the unit-cell dimensions are $a = 13{\cdot}36$, $b = 36{\cdot}24$, $c = 7{\cdot}15$ Å, $Z = 4$. The crystal structure was solved by the heavy-atom method and refined by the block-matrix least-squares method including anisotropic thermal parameters. The final R value for 1288 observed structure factors was 0·084. The absolute configuration was determined by the use of the anomalous dispersion of bromine atoms for Mo $K\alpha$ radiation. The molecular structure of bacogenin-A$_1$ was determined to be a partially modified dammarane-type triterpene.

Introduction

Bacogenin-A$_1$, $C_{30}H_{48}O_4$, is one of the sapogenins obtained on acid hydrolysis of bacoside A which was isolated from an Indian plant, *Bacopa monniera* (Kulshreshtha & Rastogi, 1973). On the basis of the chemical and spectroscopic data, bacogenin-A$_1$ was shown to be a tetracyclic triterpene having a chemical structure formulated as (I) (Fig. 1). However, an alternative formula having a methyl at C(24) could not be ruled out.

Therefore, an X-ray structure analysis of bacogenin-A$_1$ dibromoacetate (II) (Fig. 1), has been undertaken in order to establish the chemical structure of bacogenin-A$_1$ including its absolute configuration.

Experimental

Bacogenin-A$_1$ was treated with bromoacetyl bromide in chloroform containing a few drops of pyridine to give bacogenin-A$_1$ dibromoacetate. The product was recrystallized from MeOH to obtain colourless prisms

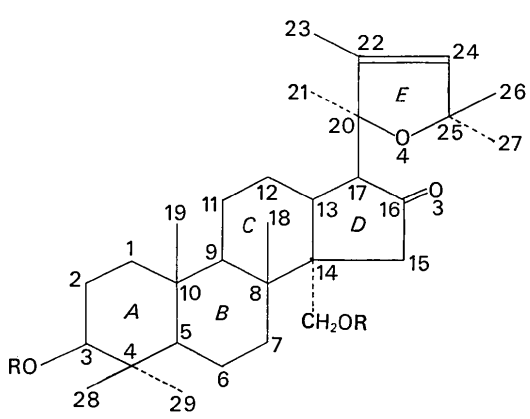

Fig. 1. Chemical formulae: (I) bacogenin-A$_1$; (II) bacogenin-A$_1$ dibromoacetate. (I) R=H; (II) R=$COCH_2Br$.