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The Structure of 1,6:8,13-Butane-1,4-diylidene[14]annulene

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The crystal and molecular structure of 1,6:8,13-butane-1,4-diylidene[14]annulene has been determined and refined by least-squares methods. The crystals are orthorhombic, space group *Fmm*2, with $a = 18·034$, $b = 11·399$, $c = 6·059$ Å and four molecules per unit cell. Intensity data for 424 reflexions were collected on a PAILRED diffractometer from crystals mounted along the c and the a axes. The final R index for 407 reflexions included in the least squares is 0·045; the average standard deviations in the atomic positions are about 0·003 Å for C atoms and 0·03 Å for H atoms. The aromatic behaviour of the compound agrees with the observed restricted misalignment between adjacent p_z orbitals along the annulene perimeter; in comparison with the corresponding propane derivative, the introduction of a further carbon atom in the aliphatic chain has negligible effects upon bond lengths in the annulene ring.

Introduction

It has been found (Vogel, Biskup, Vogel & Günther, 1966; Vogel & Günther, 1967; Vogel, Vogel, Kübbeler & Sturm, 1970; Vogel, Sturm & Cremer, 1970) that $4n+2$ bridged annulenes can show aromatic behaviour in spite of the distortion imposed by the bridges upon the annulene ring. In particular, for *syn*-bridged [14]-annulenes (Ganis & Dunitz, 1966; Casalone, Gavezzotti, Mugnoli & Simonetta, 1970; Gavezzotti, Mugnoli, Raimondi & Simonetta, 1972) the molecular symmetry is close to *mm*2 and the bond distances along the ring are all near to the benzenic value.

On the other hand, *anti*-bridged [14]annulenes, which have olefinic reactivity, show a systematic succession of 'longer' and 'shorter' bonds along the ring and a molecular symmetry close to *m* (Barrow & Mills, 1971; Gramaccioli, Mimun, Mugnoli & Simonetta, 1971). In 1,6:8,13-butane-1,4-diylidene[14]annulene, the strain imposed on the annulene ring is very severe, but this does not affect its chemical aromatic behaviour (Vogel, Sturm & Cremer, 1970).

In order to answer this problem in terms of molecular geometry and conformation, we have undertaken the study of the crystal structure of this compound. Preliminary results have been collected in a short communication (Gramaccioli, Mugnoli, Pilati, Raimondi & Simonetta, 1971).

Experimental

Crystals of 1,6:8,13-butane-1,4-diylidene[14]annulene (here onwards BUT) are in the form of orange needles,* elongated along **c**. Weissenberg photographs indicated them to be orthorhombic, in space group *Fmm*2, *Fmmm*, or *F*222 (the systematic absences being only due to the presence of the *F*-centred lattice); the first space group was confirmed by solution of the structure.

The unit-cell dimensions (see Table 1) were obtained from a least-squares fit to measurements of $\sin^2\theta$ for 40 $hk0$ and 24 $0kl$ reflexions on zero-level Weissenberg photographs taken at 21 °C with Cu $K\alpha$ radiation; the film was held in the asymmetric position, following the Straumanis technique. No corrections for eccentricity or absorption were included in least-squares calculations, and weights were assigned as inversely proportional to $\sin^2 2\theta$. The density was measured by flotation in a dilute K_2HgI_4 solution.

Table 1. *Crystal data*

$C_{18}H_{16}$
Orthorhombic
$a = 18·034 \pm 0·003$ Å
$b = 11·399 \pm 0·001$
$c = 6·059 \pm 0·002$
$Z = 4$

$D_m = 1·22$ g.cm^{-3}
$F(000) = 496$

M.W. 232·33
Space group *Fmm*2
$\lambda(\text{Cu } K\alpha_1) = 1·54051$ Å
$\lambda(\text{Cu } K\alpha_2) = 1·54433$
$\lambda(\text{Cu } K\alpha) = 1·5418$
$\mu = 5·34$ cm^{-1} (for Cu $K\alpha$)
$\mu = 0·75$ (for Mo $K\alpha$)
$D_x = 1·239$ g.cm^{-3}
$V = 1245·55$ Å^3

For the determination of the structure, intensity data were collected on a Philips equi-inclination linear diffractometer (PAILRED) in the automatic mode, using the ω-scan technique. Mo $K\alpha$ radiation [monochromated by a graphite (0001) single crystal] and a scintillation detector with pulse height analyser were used. The scan range varied from ±0·5 to ±1·2° (the larger values being used in the higher layers for low values of the Υ angle). The scan speed was 0·5°. min^{-1}; background counts were taken for 100 to 240 sec at both ends of the scan, with crystal and counter stationary. Scanning was automatically repeated for each reflexion (up to a maximum of three times), until the number of scan counts reached the value of at least 1000. The layers 0 to 7 about the c axis, the $3kl$ layer and three $00l$ reflexions for the $0kl$ layer were collected from two

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* We thank Professor Emanuel Vogel for supplying crystals of the substance.

crystals with diameters of about 0·3 mm. In total, 424 reflexions were measured and corrected for Lorentz and polarization factors. Of these, 23 were so weak that the background exceeded peak intensity: in such cases, the reflexion was assigned a value of zero. Since the X-ray tube had to be changed during data collection, and the data came from different crystals, the reflexions as collected were grouped into three sets. The evaluation of relative scale factors for these sets and the subsequent averaging of the observed F^2 values were performed according to the method proposed by Rollett and Sparks, modified to account for the dependence of the weights upon the final scale factors (Hamilton, Rollett & Sparks, 1965; Duchamp, 1964).

Determination and refinement of the structure

Because of the nature of the space group and the small number of molecules per unit cell, there are few possibilities for a plausible structure, and determination *a priori* of a possible model was attempted. To this purpose, the geometry of an isolated molecule of BUT was calculated by means of an empirically extended Westheimer method (Westheimer, 1956; Casalone,

Table 2. *Observed and calculated structure factors*

All F values have been multiplied by 10. Reflexions omitted from the least squares are indicated by an asterisk. Form factors for carbon atoms were taken from Cromer & Waber (1965) and for H atoms from Stewart, Davidson & Simpson (1965).

K	L	FO	FC	PHI
H = 0				
0	2*	1233	1459	280
0	4	225	233	173
0	6	317	315	6
2	0*	1294	1397	0
2	2	279	234	203
2	4	196	199	154
2	6	176	186	5
4	0*	657	639	180
4	2	831	763	142
4	4	279	271	172
4	6	35	37	189
6	0	106	113	0
6	2	76	67	208
6	4	390	406	215
6	6	96	101	162
8	0*	378	357	0
8	2	164	144	341
8	4	187	182	225
8	6	94	90	57
10	0	95	93	0
10	2	157	163	66
10	4	60	56	11
12	0	70	74	0
12	2	45	45	60
12	4	48	42	254
14	0	63	61	0
14	2	77	75	223
H = 1				
1	1*	1017	1029	2
1	3	61	59	44
1	5	247	263	328
1	7	94	102	328
3	1*	1200	1161	135
3	3	516	481	107
3	5	133	144	304
3	7	48	44	202
5	1	631	574	139
5	3	278	249	145
5	5	190	196	246
5	7	109	110	192
7	1	223	209	36
7	3	114	103	272
7	5	156	163	254
9	1	174	170	58
9	3	115	123	46
9	5	115	114	338
11	1	135	138	92
11	3	112	126	51
11	5	102	102	329
13	1	26	28	69
13	3	18	25	209
H = 2				
0	0*	883	924	0
0	2*	917	971	2
0	4*	342	376	282
0	6	51	52	2
2	0	108	105	0
2	2	268	263	39
2	4	171	175	226
2	6	92	99	77
4	0	49	48	180
4	2	479	441	183
4	4	343	338	169
4	6	113	114	102
6	0*	355	374	0
6	2	256	261	231
6	4	185	193	191
6	6	18	26	249
8	0*	317	308	0
8	2	104	89	272
8	4	39	43	157
8	6	76	73	356
10	0	134	139	0
10	2	0	5	186
10	4	63	69	105
12	0	89	96	0
12	2	26	34	301
12	4	41	40	215
14	0	0	13	0
14	2	35	27	218
H = 3				
1	1*	1022	1029	113
1	3	697	691	7
1	5	248	262	280
1	7	59	62	201
3	1	326	317	163
3	3	106	111	144
3	5	124	112	140
3	7	76	73	75
5	1	134	139	258
5	3	129	131	175
5	5	0	12	101
5	7	49	44	230
7	1	21	23	303
7	3	122	117	45
7	5*	148	172	318
9	1	44	34	169
9	3	90	92	91
9	5	76	78	12
11	1	40	36	304
11	3	26	33	161
11	5	30	33	73
13	1	0	14	26
13	3	39	33	327
H = 4				
0	0	443	444	180
0	2	167	157	24
0	4	229	224	341
0	6	129	129	238
2	0	0	14	0
2	2	330	308	252
2	4	117	119	126
2	6	102	99	107
4	0	237	225	0
4	2	465	432	271
4	4	235	235	150
4	6	196	188	85
6	0	34	32	0
6	2	195	201	329
6	4	104	102	340
6	6	34	36	263
8	0	144	155	180
8	2	51	51	50
8	4	80	79	357
8	6	40	38	213
10	0	44	45	180
10	2	99	97	225
10	4	101	100	146
12	0	53	58	0
12	2	88	87	281
12	4	0	26	195
14	0	0	3	0
14	2	31	34	344
H = 5				
1	1	648	634	253
1	3	123	128	158
1	5	98	93	38
1	7	188	184	222
3	1*	400	380	259
3	3	61	64	144
3	5	215	209	78
3	7	0	17	43
5	1	100	90	335
5	3	312	299	349
5	5	73	80	29
5	7	20	16	327
7	1	148	149	127
7	3	336	321	354
7	5	86	87	283
9	1	234	235	168
9	3	37	26	44
9	5	90	90	149
11	1	103	96	199
11	3	26	28	204
13	1	58	52	321
13	3	79	75	336
H = 6				
0	0	0	12	180
0	2	754	756	243
0	4	212	220	146
0	6	140	136	185
2	0	379	381	180
2	2	320	295	230
2	4	173	179	85
2	6	64	66	141
4	0	119	118	180
4	2	162	163	0
4	4	270	292	23
4	6	67	62	47
6	0	106	113	0
6	2	358	357	342
6	4	224	235	338
6	6	25	20	178
8	0	167	170	180
8	2	80	81	288
8	4	0	26	234
8	6	112	106	150
10	0	284	287	180
10	2	132	133	178
10	4	92	88	135
12	0	45	48	180
12	2	44	40	306
12	4	38	39	351
14	0	63	67	0
H = 7				
1	1	301	300	239
1	3	317	319	253
1	5	248	257	162
1	7	103	100	167
3	1	414	402	150
3	3	337	331	25
3	5	120	120	40
3	7	0	3	180
5	1	242	232	330
5	3	312	307	2
5	5	177	173	16
5	7	50	50	322
7	1*	343	332	310
7	3	163	166	274
7	5	82	86	105
9	1	218	216	210
9	3	169	167	175
9	5*	140	141	123
11	1	165	161	178
11	3	49	45	115
13	1	83	84	331
H = 8				
0	0	424	410	180
0	2	185	176	252
0	4	287	291	228
0	6*	274	267	167
2	0	859	828	180
2	2	311	299	84
2	4	109	115	326
2	6	129	121	170
4	0	275	275	180
4	2	307	308	56
4	4	327	347	14
4	6	84	81	327
6	0	383	392	0
6	2	307	308	312
6	4	119	124	7
6	6	59	59	327
8	0	79	81	0
8	2	212	210	241
8	4	108	107	136
8	6	30	32	155
10	0	258	253	180
10	2	188	187	163
10	4	96	93	105
12	0	49	49	180
12	2	34	30	22
14	0	65	77	0
H = 9				
1	1	171	152	277
1	3	200	211	234
1	5	167	172	176
1	7	31	30	149
3	1	96	86	441
3	3	74	75	72
3	5	90	92	74
3	7	67	68	25
5	1	268	271	337
5	3	78	78	331
5	5	92	93	36
7	1	231	223	321
7	3	110	107	251
7	5	32	32	135
9	1	138	136	190
9	3	134	131	165
9	5	78	80	137
11	1	77	69	177
11	3	39	41	160
13	1	98	97	340
H = 10				
0	0	21	21	0
0	2	127	118	163
0	4	34	37	27
0	6	188	184	272
2	0	0	4	0
2	2	159	164	156
2	4	92	92	90
2	6	81	82	300
4	0	73	74	0
4	2	63	68	98
4	4	54	55	76
4	6	60	55	6
6	0	0	25	0
6	2	180	175	38
6	4	145	139	314
6	6	79	76	265
8	0	183	193	180
8	2	166	172	83
8	4	86	85	305
10	0	148	146	180
10	2	111	111	119
10	4	30	26	174
12	0	45	43	0
12	2	29	28	354
H = 11				
1	1	251	246	334
1	3	153	158	169
1	5	81	85	330
3	1	272	256	316
3	3	317	314	185
3	5	143	139	121
5	1	116	121	354
5	3	122	131	209
5	5	80	86	173
7	1	136	142	90
7	3	70	70	354
7	5	120	116	255
9	1	82	83	106
9	3	33	28	162
9	5	49	43	192
11	1	77	75	340
11	3	79	74	205
H = 12				
0	0	34	29	0
0	2	378	375	62
0	4	245	259	328
0	6	218	200	287
2	0	19	18	0
2	2	204	208	92
2	4	31	47	287
2	6	71	69	305
4	0	0	29	180
4	2	162	163	143
4	4	138	146	180
4	6	0	16	76
6	0	59	60	180
6	2	158	157	100
6	4	73	72	274
8	0	17	15	180
8	2	141	137	87
8	4	61	62	322
10	0	78	75	0
10	2	39	38	103
10	4	0	21	130
12	0	65	66	0
12	2	21	20	55
H = 13				
1	1	273	284	40
1	3	160	162	331
1	5	115	111	261
3	1	106	113	109
3	3	156	164	179
3	5	106	102	168
5	1	21	23	196
5	3	232	234	182
5	5	83	80	182
7	1	127	131	335
7	3	131	124	194
7	5	35	36	273
9	1	138	141	340
9	3	81	75	177
11	1	80	76	357
H = 14				
0	0	307	317	0
0	2	264	281	8
0	4	167	182	302
0	6	80	80	337
2	0	52	54	180
2	2	197	195	75
2	4	72	75	308
2	6	49	42	328
4	0	255	262	180
4	2	273	288	134
4	4	44	48	152
6	0	0	24	0
6	2	96	102	174
6	4	72	66	206
8	0	148	161	0
8	2	0	28	290
8	4	0	3	254
10	0	44	46	0
10	2	77	71	70
H = 15				
1	1	352	359	333
1	3	112	111	245
1	5	82	73	41
3	1	151	160	158
3	3	124	129	136
3	5	24	24	70
5	1	123	125	169
5	3	106	107	178
5	5	86	75	198
7	1	106	113	334
7	3	120	110	252
9	1	65	67	17
9	3	40	42	355
11	1	59	50	91
H = 16				
0	0	408	420	0
0	2	237	242	287
0	4	79	77	44
2	0	43	41	0
2	2	53	56	213
2	4	98	97	57
4	0	241	254	180
4	2	157	155	142
4	4	39	37	81
6	0	69	72	160
6	2	0	21	317
6	4	72	74	251
8	0	0	6	180
8	2	74	75	7
10	0	61	60	180
10	2	88	77	63
H = 17				
1	1	81	91	305
1	3	84	83	340
1	5	40	40	21
3	1	106	111	189
3	3	0	20	115
3	5	59	59	107
5	1	64	63	212
5	3	51	47	264
7	1	47	37	312
7	3	73	81	317
9	1	0	16	164
H = 18				
0	0	194	193	180
0	2	131	135	27
0	4	138	136	331
2	0	148	156	180
2	2	46	41	5
2	4	41	40	354
4	0	39	42	180
4	2	89	91	260
4	4	49	50	122
6	0	26	24	0
6	2	80	86	285
8	0	0	19	180
8	2	28	25	279
H = 19				
1	1	145	140	150
1	3	131	134	355
3	1	62	58	239
3	3	30	34	303
5	1	92	92	294
5	3	40	39	327
7	1	26	37	268
H = 20				
0	0	65	69	180
0	2	66	60	236
0	4	21	23	126
2	0	12	20	180
2	2	87	75	249
4	0	57	50	0
4	2	78	75	290
6	0	0	26	0
6	2	77	68	339
H = 21				
1	1	88	88	259
1	3	85	85	176
3	1	21	19	226
3	3	42	38	73
5	1	35	41	54
H = 22				
0	0	83	77	0
0	2	124	119	233
2	0	0	16	0
2	2	50	42	201
4	0	0	3	0
H = 23				
1	1	52	47	118

Table 3. *Heavy atom parameters and their standard deviations*

All the values in this table have been multiplied by 10^4.

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

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(1)	691 (1)	1033 (2)	−9 (5)	26 (1)	61 (1)	157 (4)	−7 (1)	−4 (1)	−9 (2)
C(2)	1327 (1)	1360 (2)	−1253 (5)	30 (1)	92 (2)	231 (6)	−17 (1)	−4 (1)	21 (3)
C(3)	1894 (1)	622 (2)	−1786 (5)	23 (0)	138 (3)	253 (6)	−12 (1)	7 (2)	9 (4)
C(14)	0 (0)	1523 (2)	−496 (0)	30 (1)	49 (2)	168 (6)	0 (0)	0 (0)	6 (2)
C(15)	808 (1)	0 (0)	1498 (6)	22 (1)	74 (2)	148 (6)	0 (0)	−9 (2)	0 (0)
C(16)	421 (2)	0 (0)	3723 (6)	36 (1)	86 (2)	113 (5)	0 (0)	−10 (2)	0 (0)

Mariani, Mugnoli & Simonetta, 1968). In these calculations, at the starting point, the molecule was assumed to have point-group symmetry *2* (C_2), and all bond lengths in the ring were taken as 1·397 Å. The energy was obtained as the sum of contributions due to π-electron, stretching, bending, torsional and non-bonded interactions, using the same procedure and parameters as for 1,6:8,13-propane-1,3-diylidene[14]-annulene (here onwards PAN) (Gavezzotti, Mugnoli, Raimondi & Simonetta, 1972). The 'theoretical' molecular model corresponds to a minimum of energy, as a function of eleven internal degrees of freedom of the C-atom skeleton.† Standard values were assumed for the C–H bond lengths and the directions of these bonds were determined by orthogonality conditions for the hybrid carbon orbitals.

The minimum-energy geometry was found to correspond to *mm*2 symmetry, leading to an eclipsed conformation for the contiguous CH_2 groups.

In view of the symmetry of the molecular model, the number of molecules *Z* in the unit cell, and the nature of special positions in *Fmm*2, *Fmmm*, and *F*222 (see *International Tables for X-ray Crystallography*, 1952), only the first space group was possible. The problem, therefore, was to find which axis was polar (*i.e.* whether the space group had to be written as *Fmm*2, *Fm*2*m* or *F*2*mm*); for each of these possibilities we had to check two orientations of the molecule, turned at 90° from each other, and both with one crystallographic axis perpendicular to a given plane of symmetry of the molecule.

For these reasons, six orientations of the molecule were possible; for each, the packing energy was readily calculated using Bartell's (1960) functions. For one situation the packing energy was decidedly reasonable ($-2\cdot5$ kcal. mole^{-1}); for all the others some contacts were too short to be admissible. Using the 'theoretical' molecular model, oriented as suggested by these packing energy considerations, a structure factor calculation on all reflexions with $\sin^2\theta/\lambda^2 \le 0\cdot20$ gave an *R* index of 0·24.

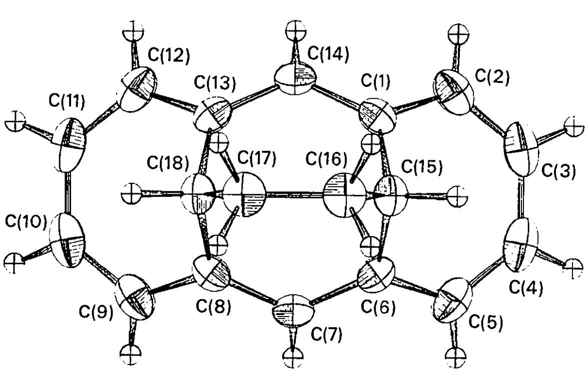

Fig. 1. The molecule of BUT showing the temperature ellipsoids of the carbon atoms. Hydrogen atoms, treated as isotropic, are on an arbitrary scale; in the present work, they are indicated by the same number as the carbon atoms to which they are bonded.

Refinement of the structure was performed by full-matrix least squares, using a program written by Busing, Martin & Levy (1962), minimizing the function $\sum w(|F|_{\text{obs}}-|F|_{\text{cal}})^2$, with weights $w=1/\bar{f}^2$, where $\bar{f}$ is the average scattering factor for all the atoms at the calculated value of $\sin\theta/\lambda$. In the first three cycles, performed on those reflexions for which $I\ge 2\sigma(I)$, only the carbon atoms were considered, with isotropic temperature factors; the *R* index dropped to 0·125. After these cycles, anisotropic temperature factors were assigned to the carbon atoms; the hydrogen atoms were included in the structure factor calculations with a temperature factor *B* of 4 Å^2 (for four atoms, whose coordinates were deduced from a three-dimensional difference Fourier) or 5 Å^2 [for H(2) and H(5), whose coordinates were taken from the 'theoretical' molecular model]. After three additional cycles of least squares, performed minimizing the same expression as before with the same weights and the same reflexions, the *R* index dropped to 0·049.

At this stage hydrogen atom parameters were also considered in the refinement, and three final cycles of least squares were computed. Here, all the measured reflexions were included, with the exception of 17, for which either the effects of secondary extinction were evident ($F\ge 90$), or some substantial disagreement was found between different observations during our data reduction. All these reflexions are marked by an asterisk in the structure factor table. Owing to the fact that different crystals were used, no secondary extinction coefficient was considered in the refinement.

In these final cycles, weights were assigned as $w=1/\sigma^2(F)$, where $\sigma(F)$ was taken as $\sigma(F^2)/2F$ and computed from $\sigma^2(F^2)=\sigma^2_{cs}(F^2_o)+(AF^2_o)^2$. Here, $\sigma^2_{cs}(F^2_o)$ is the counting statistical variance and *A* an empirical parameter, which was chosen so as to make $w(\Delta F)^2$, the mean quadratic error, approximately constant over the entire range of $|F_o|$'s (Peterson & Levy, 1959; Cruickshank & Pilling, 1961; Albano, Bellon, Chini & Scatturin, 1969). During our choice of the empirical parameter *A*, the reflexions were divided into three groups, each containing the same number of data. The value of $A(=0\cdot11)$ which gave the best results from this point of view [constancy of $w(\Delta F)^2$ within 6·5% of the average] gave also a reasonable 'goodness of fit' $s=\sqrt{[\sum w(\Delta F)^2/n-p]}=1\cdot18$, a result which induced us to consider this scheme of weighting with particular favour.

After three cycles, the *R* index was reduced to 0·045 for the reflexions included in the least-squares calculations and reasonable shifts were found for all the hydrogen atom parameters. At the end of the refinement, no shift in either the atomic coordinates or the temperature factors exceeded $\frac{1}{20}$ of the corresponding

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† The two extra degrees of freedom with respect to those considered in the calculations for PAN are the bond length C(16)–C(17) and the torsion angle around this bond.

Table 4. *Parameters for the hydrogen atoms*

	x	*y*	*z*	10 *B*(Å²)
H(2)	0·135 (1)	0·214 (2)	−0·189 (7)	66 (7)
H(3)	0·236 (2)	0·094 (2)	−0·241 (7)	65 (6)
H(14)	0·000 (0)	0·208 (2)	−0·155 (8)	40 (7)
H(15)	0·135 (1)	0·000 (0)	0·195 (6)	45 (6)
H(16)	0·064 (1)	0·068 (2)	0·452 (4)	53 (7)

standard deviation, with the exception of *B* for H(15), whose shift was $\frac{1}{10}$ of the corresponding σ. Owing to the small shifts in the atomic coordinates, the goodness of fit decreased slightly (to 1·10), the final value being then considered as satisfactory. A general view of the molecule is given in Fig. 1.

Precision of the results

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

The standard deviations in the coordinates of the heavier atoms, derived from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle, correspond to positional uncertainties of the order of 0·003 Å for the carbon atoms and 0·03 Å for the hydrogen atoms. The corresponding standard deviations in the bond distances involving only heavier atoms are about 0·004 Å and in the angles about 0·3°; in the C–H bonds they are about 0·03 Å and in the angles involving H-atoms they are about 2°.

Corrections for thermal libration

A molecule such as BUT was expected to behave as a rigid body in undergoing thermal libration. Accordingly, the tensors **T**,**L**,**S** (Schomaker & Trueblood, 1968) were derived from a least-squares treatment, using a FORTRAN IV program written by Dr Giuseppe Filippini. In these calculations, equal weights were assigned to all thermal factors; owing to the *mm*2 crystallographic symmetry of the molecule, the off-diagonal components of **T** and **L** and all components of **S**, except S_{12} and S_{21} were bound to be zero. The agreement between observed and calculated B_{ij} values was good, only the values for B_{11} of C(5) differing by slightly more than three times the standard deviation.

The mean square rotational displacements of BUT amount to 15,13 and 7 $(°)^2$ about the principal axes of the tensor **L**.

Bond distances and angles involving C atoms are reported in Table 5; values in the third column include corrections for thermal motion. For this purpose, corrections were derived from the formula proposed by Schomaker & Trueblood (1968), using the rigid-body parameters of Table 6. Corrections to the bond angles are very small (less than 0·05°) and have been neglected.

Table 5. *Bond distances and angles*

	Data for BUT (this work)			Average for PAN	
	Uncorrected for thermal libration	Corrected	'Theoretical'	Corrected thermal libration	'Theoretical'
C(1)—C(2)	1·422 Å	1·428 Å	1·397 Å	1·413 Å	1·397 Å
C(2)—C(3)	1·362	1·368	1·397	1·387	1·397
C(3)—C(4)	1·418	1·424	1·397	1·414	1·397
C(14)-C(1)	1·397	1·402	1·397	1·395	1·397
C(1)—C(15)	1·505	1·511	1·474	1·517	1·487
C(15)-C(16)	1·518	1·523	1·531	1·518	1·533
C(16)-C(17)	1·519	1·525	1·493	not comparable	

	Data for BUT		Data for PAN	
	(Correction for thermal libration negligible) Experimental	'Theoretical'	Experimental	'Theoretical'
C(14)-C(1)—C(2)	120·2°	120·6°	124·0°	124·1°
C(1)—C(2)—C(3)	124·7	122·5	121·5	118·6
C(2)—C(3)—C(4)	128·1	129·1	127·9	127·5
C(6)—C(7)—C(8)	126·2	120·8	121·5	118·6
C(2)—C(1)—C(15)	114·4	115·1	119·2	119·7
C(14)-C(1)—C(15)	124·5	124·3	116·6	116·2
C(1)—C(15)-C(16)	118·3	117·7	111·2	110·6
C(15)-C(16)-C(17)	117·4	116·2	not comparable	
C(1)—C(15)-C(6)	102·9	105·8	104·3	105·8
Torsion angles				
C(14)-C(1)—C(2)-C(3)	−144·6°	−153·7°	−151·8°	−162·7°
C(1)—C(2)—C(3)-C(4)	18·6	16·8	20·9	25·5
C(13)-C(14)-C(1)-C(2)	156·4	147·5	164·6	158·1

Distances and angles involving the hydrogen atoms (uncorrected for thermal libration) are shown in Table 7. Torsion angles are reported in Table 5; signs for these angles are given following the convention proposed by Klyne & Prelog (1960); the standard deviations were calculated according to Huber (1961).

Discussion

In agreement with its chemical behaviour, the molecule of BUT clearly shows an aromatic character, the C–C bond distances along the annulene perimeter varying from 1·371 to 1·422 Å, a range which is narrower than that found for anthracene (1·366–1·433 Å).

Of these bond distances, each one is virtually identical (see Table 6) with the average of the corresponding bond distances, as found in PAN (assuming molecular symmetry *mm*2 also for the latter). This confirms the significant variation of C–C bond lengths which is observed along the annulene perimeter in this series of compounds.

With respect to PAN, the strain connected with the presence of a further carbon atom in the aliphatic chain seems to affect bond angles much more than bond lengths, the observed variation from PAN to BUT being fairly consistent with theoretical results (see Tables 5 and 8).

Molecular packing

If we assume as van der Waals radii for carbon and hydrogen the values 1·7 and 1·5 Å respectively, we see that only in a few cases do two atoms belonging to different molecules lie at a distance smaller than the sum of the corresponding van der Waals radii (see Table 9).

Table 6. *Rigid-body tensors for BUT*

The tensors are referred to a Cartesian coordinate system, with the same orientation as the crystallographic axes. All values have been multiplied by 10^4.

T(Å^2)	369 (8)	0	0	
		326 (10)	0	('unreduced')
			203 (10)	
L(rad^2)	39 (4)	0	0	
		23 (1)	0	
			48 (2)	
S(Å. rad)	0	−4 (4)	0	
	17 (2)	0	0	
	0	0	0	

Table 9. *Intermolecular contact distances*

(Uncorrected for thermal libration.)

C(1)—H(2)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	3·05 Å
C(2)—H(2)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	3·15
C(2)—H(16)	$x, y, z-1$	2·95
C(3)—H(3)	$\frac{1}{2}-x, y, z-\frac{1}{2}$	3·68
C(3)—H(3)	$\frac{1}{2}-x, y, \frac{1}{2}+z$	2·99
C(3)—H(16)	$x, y, z-1$	3·19
C(14)–H(14)	$x, \frac{1}{2}-y, \frac{1}{2}+z$	2·87
H(2)—H(16)	$x, \frac{1}{2}-y, z-\frac{1}{2}$	2·93
H(3)—H(15)	$\frac{1}{2}-x, y, z-\frac{1}{2}$	2·58
H(14)–H(16)	$x, \frac{1}{2}-y, z-\frac{1}{2}$	2·87
H(14)–H(16)	$-x, \frac{1}{2}-y, \frac{1}{2}+z$	2·87

Table 7. *Bond distances and angles involving hydrogen atoms* (*uncorrected for thermal libration*)

C(2)—H(2)	0·97Å	C(15)–H(15)	1·02 Å
C(3)—H(3)	1·00	C(16)–H(16)	0·99
C(14)–H(14)	0·90		
C(1)–C(2)—H(2)	119°	C(1)—C(15)–H(15)	107°
C(3)–C(2)—H(2)	116	C(16)–C(15)–H(15)	102
C(2)–C(3)—H(3)	120	C(15)–C(16)–H(16)	105
C(4)–C(3)—H(3)	111	C(17)–C(16)–H(16)	113
C(1)–C(14)–H(14)	116	H(16)–C(16)–H(16′)	103

Table 8. *Some planes of interest*

Because of the nature and special symmetry of the molecule, the atoms in all these planes are strictly coplanar, even if there are more than three. The coefficients q_i are the direction cosines relative to the crystallographic axes **a**, **b**, and **c**.

Plane	q_1	q_2	q_3	D
A [C(2)-C(3)-C(4)-C(5)]	−0·3015	0·0000	−0·9535	−0·002 Å
B [C(1)-C(2)-C(5)-C(6)]	0·5489	0·0000	0·8359	−0·679
C [C(1)-C(6)-C(7)-C(14)]	0·2304	0·0000	−0·9731	−0·292
D [C(1)-C(6)-C(15)]	0·9742	0·0000	−0·2258	−1·215
C′ [C(7)-C(8)-C(13)-C(14)]	−0·2304	0·0000	−0·9731	−0·292

Dihedral angles

	BUT		PAN	
	Experimental	'Theoretical'	Experimental	'Theoretical'
A∧B	164·3°	165·2°	162·4°	158·2°
B∧C	133·4	140·8	139·6	144·3
B∧D	110·2	109·7	114·4	113·8
C∧D	116·4	109·5	106·0	101·9
C∧C′	153·4	168·0	148·6	158·9

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The Crystal Structure of β-D-Galactosamine Hydrochloride

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The crystal structure of β-D-galactosamine hydrochloride has been determined from three-dimensional intensities obtained with Cu $K\alpha$ radiation. The needle-shaped crystals are orthorhombic, space group $P2_12_12_1$, with eight molecules in a unit cell of dimensions $a=9{\cdot}794$, $b=19{\cdot}686$ $c=9{\cdot}385$ Å. The final R index is 0·045 and the e.s.d.'s of the coordinates of C, N and O atoms are about 0·005 Å. Bond lengths and angles in galactosamine are very close to those of similar compounds already reported. The galactosamine ring has the normal Sachse *trans* configuration with 1*e*2*e*3*e*4*a*5*e*.

Introduction

D-Galactosamine (2-amino-2-desoxy-D-galactose or chondrosamine) is one of the important amino-sugars. It is a constituent of complex polysaccharides, glucoprotein of mucoid, mucin and chondroitin sulphate. In most of these compounds, D-galactosamine occurs together with glucosamine. The crystal structures of α-D-glucosamine hydrochloride and hydrobromide have been determined by Chu & Jeffrey (1965). In this structure, the glucopyranose ring has the normal Sachse *trans* configuration with lower energy conformation 1a2e3e4e5e. The preliminary studies on β-D-galactosamine hydrochloride have been reported by Werner (1952). The crystal structure, however, was still undetermined. In view of its relation to other pyranose sugars and biochemical interest, it was of interest to determine the conformation of the galactopyranose ring in this compound.

Experimental

The crystals of β-D-galactosamine hydrochloride were recrystallized from aqueous acetone solution. They are