individual values of bond lengths and bond angles from their group averages give a basis for further study.

It is a pleasure to express our indebtedness to Dr W. H. Taylor for suggesting this work, and for his support and guidance throughout its execution. It will be obvious how much it owes to his forethought and wise planning, by which detailed structural studies of the key members of the felspar family have been made available for comparison with each other. We are grateful to Mr P. H. Ribbe for carrying out the bond angle calculations.

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The Molecular and Crystal Structure of 3-Benzoylanthranil (2-Phenylisoisatogen)

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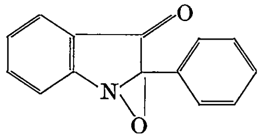
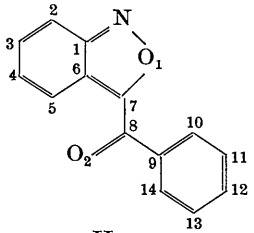
The crystal structure investigation of a compound ($C_{14}H_9NO_2$), previously known as 2-phenylisoisatogen, has established its chemical constitution to be that of 3-benzoylanthranil, (or 3 benzoyl 2,1-benzisoxazole). The structure was solved by means of a well-resolved projection down a short axis and was refined with three-dimensional data using differential syntheses and least squares methods. The hydrogen atoms were located by difference syntheses. The configuration of the molecule and the bond lengths are discussed in terms of valence-bond resonance theory.

Introduction

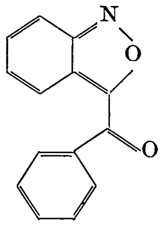
Ruggli (1919) and Ruggli, Caspar & Hegedus (1939) assigned the tricyclic oxide bridge structure, I, to 2-phenylisoisatogen, the isomer obtained by treating 2-phenylisatogen (Baeyer, 1882) with hot methanolic H_2SO_4. A re-examination of this structure by Cohen & Pinkus (1959) cast doubt on the validity of the Ruggli formulation. The more plausible structure, II, was proposed, for which a planar or nearly planar molecule might be resonance stabilized *cis* or *trans* with respect to the central C_7–C_8 bond. This X-ray investigation was initially undertaken to verify this formulation and to decide between the two possible stereo-isomers, II or III. It became possible at an early stage in the analysis to identify the molecule as II, which is 3-benzoylanthranil and this was briefly reported by Pinkus, Cohen, Sundaralingam & Jeffrey (1960). A more detailed study was then pursued because of the interest in the detailed stereochemistry of the molecule and its interpretation in terms of resonance theory.



I



II



III

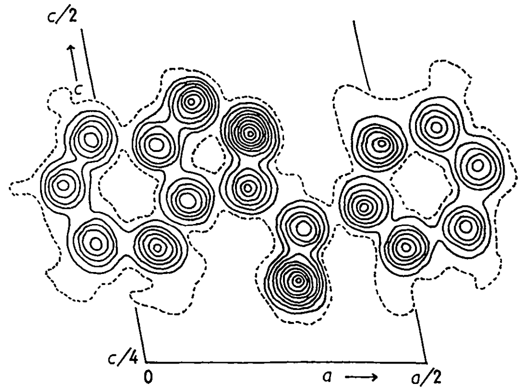


Fig. 1. Fourier projection on (010).
Contour intervals 1 e.Å^{-2}, zero omitted, first broken.

Experimental

Monoclinic single crystals of 3-benzoylanthranil elongated along the b axis with well-developed faces on $\{001\}$, $\{\bar{2}01\}$ and $\{\bar{3}01\}$ were obtained from ethanol solution. The cell constants were measured from Weissenberg photographs, using the Straumanis method, as

$$a=12\cdot391\pm0\cdot015,\ b=3\cdot892\pm0\cdot02,\ c=23\cdot001\pm0\cdot02\ \text{Å};\quad \beta=100°\ 48'\pm15'.$$

The space group was deduced as $P2_1/c$, from the systematic extinctions ($h0l$) absent for l odd, ($0k0$) absent from k odd. With $Z=4$, $D_x=1\cdot36$ g.cm.$^{-3}$; $D_m=1\cdot34$ g.cm.$^{-3}$, by flotation in aqueous solutions of $BaCl_2$.

The intensities were measured by eye-estimation from multiple-film Weissenberg photographs taken with Cu $K\alpha$ radiation. The zero to three layers about the b axis and zero to six layers about the a axis were recorded. The intensities were reduced to structure amplitudes by Shiono's (1959) IBM 650 data reduction program. The layers were scaled both by the common reflections and by comparison with the calculated structure factors when a good trial structure had been obtained. The scale factors from both methods agreed within 2%. 1024 independent structure amplitudes were observed. No corrections were made for absorption and there was no evidence of extinction.

The projection analysis

The initial x and z coordinates were obtained by fitting the structure II on trial Fourier maps based on signs obtained from Harker–Kasper inequalities and molecular packing considerations. The unitary structure factors were accidentally calculated with twice the proper scale factors, and in effect the 'hit-or-miss' method (Woolfson, 1961) was used. Although 15 of the 32 signs initially deduced were subsequently shown to be incorrect, the signs of the four strongest reflections were correctly determined and these mainly determined the molecular orientation; the projection converged to a true solution very rapidly by ordinary Fourier and difference Fourier methods. The agreement index, R, for the $h0l$ reflections was 0·15 for the coordinates taken from the Fourier projection which is shown in Fig. 1. The good agreement and resolution in the electron density map and with the correct relative heights of the carbon, nitrogen and oxygen atoms established the chemical constitution of 2-phenylisoisatogen as 3-benzoylanthranil, with the oxygen atoms *trans* related as in II. At this stage in the analysis, it was believed that the molecule was very nearly planar and that the shortening of some of the bond lengths in projection could be accounted for by tilting the whole molecule in one plane.

The three-dimensional analysis and refinement

The ($hk0$) Patterson projection indicated that the mean plane of the molecule was tilted about 27° to (010). Assuming a planar model with normal distances and angles, a set of trial y coordinates was obtained which satisfied the strongest (hkl) reflections and gave acceptable intermolecular separations of greater than 3·0 Å.

Successive structure factor and Fourier and difference Fourier calculations reduced the R factor to 0·14 for all observed reflections with a uniform isotropic temperature factor of $B=3\cdot7$ Å^2. The hydrogen atom contributions were included at calculated positions 1·08 Å, from the associated carbon atom and with the same temperature factor.

An isotropic least squares calculation with individual temperature factors was computed on the IBM 704 using the Busing & Levy (1959) program. This reduced R to 0·11. A final cycle of least squares anisotropic refinement with the same program reduced R to 0·09, and gave the atomic parameters shown in Table 1. In the least squares calculations, the Hughes (1941) weighting scheme was used and the unobserved

Table 1.

The atomic parameters

	x/a	y/b	z/c
C_1	0·0744	0·2239	0·4186
C_2	−0·0341	0·1727	0·4344
C_3	−0·1026	0·0256	0·3777
C_4	−0·0665	−0·0866	0·3253
C_5	0·0416	−0·0451	0·3199
C_6	0·1135	0·1187	0·3669
C_7	0·2234	0·2190	0·3774
C_8	0·3065	0·1928	0·3394
C_9	0·4257	0·2871	0·3628
C_{10}	0·4761	0·2401	0·4220
C_{11}	0·5862	0·3260	0·4411
C_{12}	0·6462	0·4536	0·4014
C_{13}	0·5988	0·5034	0·3431
C_{14}	0·4870	0·4146	0·3223
O_1	0·2473	0·3683	0·4316
O_2	0·2777	0·0988	0·2882
N	0·1533	0·3773	0·4581

The standard deviation varied from 0·004 to 0·007 Å, with a mean value of 0·0064 for the carbons, 0·0047 for the oxygens, and 0·0058 for the nitrogen.

The anisotropic thermal parameters (Å^2)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C_1	3·2	3·4	3·5	0·1	0·3	0·2
C_2	3·1	4·5	4·7	0·2	0·4	0·2
C_3	3·4	3·2	5·2	0·0	0·5	0·2
C_4	3·9	3·9	4·7	0·1	0·4	0·0
C_5	3·6	3·2	3·3	0·0	0·2	−0·1
C_6	3·3	2·3	3·4	−0·1	0·4	0·2
C_7	3·5	3·4	3·2	0·1	0·4	0·0
C_8	3·8	3·5	3·0	0·0	0·2	0·0
C_9	3·0	2·7	4·1	0·1	0·5	0·0
C_{10}	3·8	3·7	3·2	0·1	0·4	0·1
C_{11}	3·0	4·5	3·6	0·0	0·3	−0·1
C_{12}	3·5	3·9	5·1	−0·2	0·7	−0·3
C_{13}	3·6	4·6	5·2	−0·3	0·9	0·2
C_{14}	4·6	4·2	3·3	0·1	0·6	0·1
O_1	3·6	5·0	3·1	0·0	0·4	−0·5
O_2	3·5	6·8	3·5	0·1	0·2	−0·5
N	3·4	5·8	3·7	0·1	0·4	−0·5

The standard deviations for the principal terms varied from 0·22 to 0·33 with a mean value of 0·29, and for the cross terms varied from 0·08 to 0·13 with a mean value of 0·105.

reflections were omitted. The hydrogen atoms were included at calculated positions with the same isotropic temperature factors as were obtained for their carbon atoms at the conclusion of the isotropic cycle of refinement. These parameters were fixed and not varied in the refinement.

Difference syntheses were computed at the conclusion of the isotropic refinement using both the two-dimensional ($h0l$) data and the three-dimensional data with structure factors for which $\sin\theta \le 0·5$. The structure factors were calculated with isotropic temperature factors with the hydrogen atoms omitted. The only significant features on these syntheses were the residual hydrogen peaks, shown in Figs. 2 and 3. The H_3 peak in Fig. 2 is distorted by overlap by the hydrogen projected from an adjacent molecule.

The observed hydrogen parameters are compared with the calculated values used in the least squares

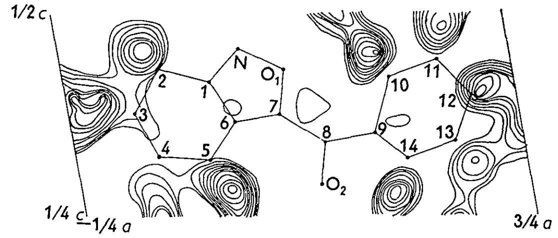


Fig. 2. ΔF synthesis projected down b axis. Contours at intervals of 0·05 e.Å^{-2}; zero, 0·05 and negative contours omitted. Only F_o's used with $\sin\theta \le 0·5$.

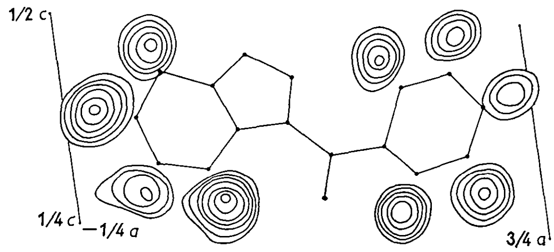


Fig. 3. A composite ΔF synthesis showing hydrogen atoms. Contours at intervals of 0·05 e.Å^{-3}, beginning from 0·1 Å. Only F_o's used with $\sin\theta \le 0·5$.

cycles in Table 2. The differences are not significant in terms of the standard deviations.

The observed and calculated structure factors (obtained from the parameters in Table 1 and the calculated hydrogen parameters in Table 2), are given in Table 3. The unobserved amplitudes are omitted.

The bond lengths and angles and their standard deviations are given in Table 4, see also Fig. 4.

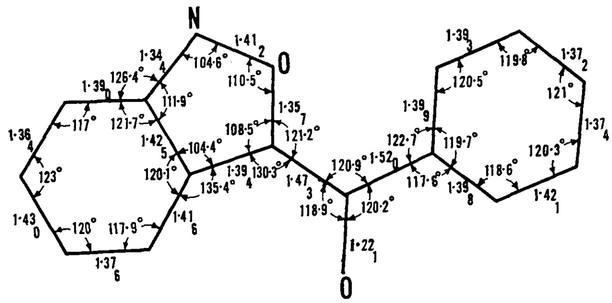


Fig. 4. Bond lengths and bond angles.

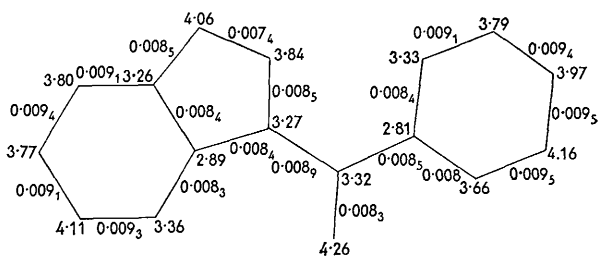


Fig. 5. The individual isotropic temperature factors and standard deviations in bond-lengths.

Table 2. *The calculated and observed hydrogen coordinates*

	x/a		y/b		z/c	
	calc.	obs.	calc.	obs.	calc.	obs.
H_2	−0·065	−0·051	0·225	0·292	0·463	0·462
H_3	−0·187	−0·190	0·002	0·008	0·382	0·383
H_4	−0·126	−0·106	−0·189	−0·217	0·290	0·289
H_5	0·073	0·069	−0·107	−0·067	0·281	0·279
H_{10}	0·429	0·434	0·127	0·092	0·452	0·457
H_{11}	0·620	0·605	0·316	0·367	0·487	0·486
H_{12}	0·735	0·704	0·510	0·383	0·417	0·415
H_{13}	0·647	0·623	0·612	0·595	0·314	0·297
H_{14}	0·450	0·438	0·430	0·467	0·277	0·273

Table 3. *Observed and calculated structure factors*

The running indices are h and l, and the value of k immediately precedes the group
The central column is $10|F_o|$, the right hand column $10F_c$. Unobserved reflections are omitted

0			
0	4	952	1308-
0	6	120	124-
0	10	177	190-
0	12	45	58
0	14	206	199
0	16	173	170
0	20	215	219-
0	24	105	104
0	28	45	45
1	4	45	46-
1	6	204	232
1	10	257	223
1	12	328	355-
1	14	238	233-
1	16	214	212
1	18	44	43-
1	20	96	80-
2	0	406	383
2	2	235	264
2	6	313	307
2	8	223	193-
2	10	76	67-
2	12	295	330
2	14	137	147-
2	16	42	49
2	18	149	161-
2	20	184	161-
2	22	167	179
3	0	45	32
3	6	199	177-
3	8	72	70
3	10	248	223
3	12	332	341
3	14	94	106
3	16	74	54-
3	18	45	50
3	20	203	192-
4	0	76	76
4	2	369	318-
4	4	114	123-
4	8	418	413-
4	12	95	88
4	14	149	206
4	16	126	91
5	0	333	283-
5	2	658	670
5	4	30	13-
5	6	88	101-
5	8	268	269-
5	10	203	205-
5	16	156	169
5	24	78	61-
6	0	506	472-
6	2	333	337-
6	4	203	220
6	6	61	57-
6	10	129	134
6	12	187	191
6	14	313	286-
6	16	187	174-
6	18	76	81
7	2	50	37
7	6	111	99
7	8	204	186
7	10	233	235-
7	12	110	112-
7	14	167	165
7	16	181	174-
7	20	104	91
7	22	76	10-
8	4	191	192-
8	6	42	37-
8	8	62	48
8	10	180	185
8	18	114	99-
9	0	135	129-
9	2	162	136
9	4	115	125-
9	6	89	74
9	8	314	310
9	10	100	80-
9	12	118	105-
9	14	72	64-
9	18	55	43
10	2	100	92-
10	4	202	198-
10	6	78	73-
10	8	235	214
10	10	44	47
10	16	69	53-
10	18	58	48
11	0	132	129-
11	4	73	80-
11	6	109	83-
11	8	60	72
11	10	88	78
11	14	61	59
11	16	86	81-
12	4	121	129-
13	4	65	57
13	10	94	74-
14	4	64	54
14	8	50	47
-1	2	511	527-
-1	6	330	401-
-1	12	187	183-
-1	18	96	94-
-1	20	151	146-
-1	22	178	181
-1	24	89	85
-2	2	289	286-
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-2	6	58	68
-2	8	378	383-
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-2	14	111	120-
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-2	22	109	97
-2	24	60	54-
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-3	12	144	137
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-3	20	334	386
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-3	24	121	130-
-4	4	511	537
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-4	22	132	140-
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-5	12	51	52-
-5	16	99	88-
-5	18	77	78-
-5	20	78	78
-5	24	126	103-
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-6	4	221	223
-6	6	292	260
-6	10	51	37
-6	12	66	57
-6	14	155	164-
-6	16	74	72-
-6	18	121	129-
-6	20	97	91
-7	2	98	101-
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-7	8	217	208-
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-7	14	95	104
-7	16	105	81
-7	18	91	91
-7	20	111	135
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-8	10	209	184-
-8	12	227	247-
-8	14	125	103
-8	16	171	184
-8	18	133	150
-9	4	241	230-
-9	6	261	281-
-9	8	250	227
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-9	12	89	111-
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-9	18	124	155-
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-10	8	45	29-
-10	10	221	201-
-10	12	90	83-
-10	14	107	116
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-12	8	118	124-
-12	10	133	137-
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-12	18	51	52
-12	22	41	44-
-13	10	71	55
-13	14	91	81-
-13	16	48	51-
-13	20	48	35
-15	12	34	25
1			
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0	4	620	697
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0	6	72	69
0	7	128	120-
0	8	83	81-
0	9	286	295-
0	10	74	88-
0	12	315	333-
0	13	95	99
0	14	59	65-
0	15	97	94-
0	16	169	171
0	18	79	85
0	19	81	71
1	0	898	890-
1	1	887	886-
1	2	170	133-
1	4	508	581
1	5	218	222
1	6	117	114-
1	7	84	80-
1	8	102	68-
1	10	206	225
1	11	257	274-
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2	3	149	154
2	4	297	288
2	5	283	317
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2	7	197	190
2	9	125	142
2	10	156	143-
2	11	129	129-
2	14	120	115
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2	20	101	110-
3	0	183	167
3	1	28	24-
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3	3	152	161-
3	4	65	61
3	5	398	431-
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3	7	93	101
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3	9	244	250
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3	18	89	74
3	20	80	82
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4	5	200	187-
4	6	52	43
4	7	66	58
4	8	53	55-
4	10	137	149-
4	11	116	95-
4	12	146	143-
4	15	75	77
4	16	100	117
4	17	87	106
5	0	250	256-
5	1	271	262
5	2	38	37-
5	3	39	39-
5	4	274	300
5	5	86	89-
5	6	88	82
5	7	45	52-
5	8	41	37
5	11	205	235-
5	13	74	84
5	14	185	212-
5	15	84	80
5	18	70	58
5	19	76	73
5	20	65	61
6	0	319	331
6	2	162	167-
6	3	179	193-
6	4	163	148-
6	5	114	136
6	6	53	46
6	9	78	86
6	10	95	93-
6	12	139	160
6	13	191	222-
6	14	142	169
6	16	142	130-
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7	1	88	79
7	2	47	45
7	3	42	30
7	4	168	165-
7	7	88	93
7	8	127	158
7	10	91	87
7	12	142	110-
8	0	140	134
8	2	115	108
8	3	64	58
8	4	107	99-
8	5	119	136
8	6	80	74-
8	7	164	154-
8	8	94	99-
8	9	83	78-
8	11	114	124
8	12	96	108
8	16	64	72
9	1	55	41-
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9	5	152	167
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2	5	189	193-
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2	7	211	228-
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2	10	144	146
2	11	84	80
2	12	58	48
2	14	41	28-
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3	1	41	35
3	2	24	14-
3	3	70	71
3	4	101	90
3	5	93	79
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3	7	48	52-
3	8	164	166-
3	9	56	52-
3	10	92	59
3	14	81	87
3	15	66	63-
3	16	45	35
3	18	60	64-
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4	5	101	99-
4	6	54	68
4	8	65	59-
4	9	105	108
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4	12	34	42
5	0	30	26
5	1	71	66-
5	4	45	37
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5	11	67	67
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6	1	46	37-
6	3	46	38-
6	8	73	51
7	0	58	57
7	1	98	88-
7	2	33	34
7	3	65	60-
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7	7	53	45
7	8	57	61-
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-10	6	81	92-
-10	11	40	37-

Table 4

The bond-lengths and standard deviations

C_1–C_2	1·390 Å	C_7–C_8	1·473 Å
C_2–C_3	1·364	C_8–O_2	1·221
C_3–C_4	1·430	C_8–C_9	1·520
C_4–C_5	1·376	C_9–C_{10}	1·399
C_5–C_6	1·416	C_{10}–C_{11}	1·393
C_6–C_1	1·425	C_{11}–C_{12}	1·372
C_1–N	1·344	C_{12}–C_{13}	1·374
N–O_1	1·412	C_{13}–C_{14}	1·421
O_1–C_7	1·357	C_{14}–C_9	1·398
C_6–C_7	1·394		

The standard variations varied from 0·007 to 0·009 with a mean value $0{\cdot}009_0$ for the C–C bonds, $0{\cdot}008_7$ for the C–N bond, $0{\cdot}008_4$ for the C–O bonds and $0{\cdot}007_4$ for the O–N bond.

C_2–H	1·04 Å	C_{11}–H	1·02 Å
C_3–H	1·12	C_{12}–H	0·78
C_4–H	1·02	C_{13}–H	1·20
C_5–H	1·06	C_{14}–H	1·21
C_{10}–H	1·19		

The standard deviation of the C–H bonds was about 0·15 Å.

The bond angles

C_1–C_2–C_3	117·0°	C_6–C_7–C_8	130·3°
C_2–C_3–C_4	123·0	O_1–C_7–C_8	121·2
C_3–C_4–C_5	120·0	C_7–C_8–O_2	118·9
C_4–C_5–C_6	117·9	C_7–C_8–C_9	120·9
C_5–C_6–C_1	120·1	O_2–C_8–C_9	120·2
C_6–C_1–C_2	121·7	C_8–C_9–C_{10}	122·7
C_1–C_6–C_7	104·4	C_8–C_9–C_{14}	117·6
C_6–C_1–N	111·9	C_9–C_{10}–C_{11}	120·5
C_1–N–O_1	104·6	C_{10}–C_{11}–C_{12}	119·8
N–O_1–C_7	110·5	C_{11}–C_{12}–C_{13}	121·0
O_1–C_7–C_6	108·5	C_{12}–C_{13}–C_{14}	120·3
C_2–C_1–N	126·4	C_{13}–C_{14}–C_9	118·6
C_5–C_6–C_7	135·4	C_{14}–C_9–C_{10}	119·7

The standard deviations increase with the distance from the center of the molecule. This is the result of the thermal motion, which was greater for the atoms at the perimeter of the molecule, and is consistent with a rigid-body angular thermal oscillation, see Fig. 5. However the molecule is not planar and it seemed likely that some independent oscillation of the two ring systems about the central C–C bond would be a significant feature of the thermal motion. No attempt was therefore made to analyze the thermal parameters quantitatively using the rigid-body approximation. Correspondingly no corrections could be made to the bond lengths for the apparent shortening due to thermal oscillations. These are estimated at 0·01 Å for the most extreme case, which was for the C=O bond.

Discussion of the structure

(a) *The planarity*

In detail the whole molecule is far from planar, but it can be described in individual parts which are planar within the accuracy of the analysis. These parts are the quinoid ring, $C_1 \cdots C_6$, the isoxazole ring C_1, C_6, C_7, O_1, N, the carbonyl group C_7, C_8, C_9, O_2, and the phenyl ring $C_9 \cdots C_{14}$. The quinoid ring and isoxazole ring taken together form the anthranil ring system.

Table 5. *The equations of the planes with respect to the orthogonal crystallographic axes a, b, c′ and the deviations from the planes in Å*

Quinoid plane $C_1 \cdots C_6$

$$-0{\cdot}1576x+0{\cdot}8969y-0{\cdot}4763z=3{\cdot}0030$$

Atoms included		Atoms omitted	
C_1	0·004 Å	C_7	0·056 Å
C_2	−0·014	C_8	0·134
C_3	0·011	C_9	0·028
C_4	0·004	C_{10}	−0·748
C_5	−0·014	C_{11}	−0·827
C_6	0·010	C_{12}	−0·154
		C_{13}	0·619
		C_{14}	0·706
		O_1	0·059
		O_2	0·306
		N	0·043

Isoxazole plane $C_1C_6C_7O_1N$

$$-0{\cdot}1832x+0{\cdot}8886y-0{\cdot}4205z=3{\cdot}0518$$

Atoms included		Atoms omitted	
C_1	−0·002 Å	C_2	0·015 Å
C_6	−0·002	C_3	0·069
C_7	0·005	C_4	0·058
O_1	−0·007	C_5	0·004
N	0·005	C_8	0·060
		C_9	−0·087

Anthranil plane $C_1 \cdots C_6$, C_7O_1N

$$-0{\cdot}1703x+0{\cdot}8925y-0{\cdot}4176z=3{\cdot}0178$$

Atoms included		Atoms omitted	
C_1	−0·017 Å	C_8	0·081 Å
C_2	−0·018	C_9	−0·046
C_3	0·023	O_2	0·262
C_4	0·015		
C_5	−0·020		
C_6	−0·012		
C_7	0·014		
O_1	0·009		
N	0·006		

Carbonyl plane C_7, C_8, C_9, O_2

$$-0{\cdot}1360x+0{\cdot}9474y-0{\cdot}2898z=1{\cdot}8278$$

Atoms included		Atoms omitted	
C_7	0·002 Å	C_6	−0·121 Å
C_8	−0·006	O_1	0·188
C_9	0·002	C_5	−0·323
O_2	0·002	C_{10}	−0·610
		C_{14}	0·612

Phenyl plane $C_9 \cdots C_{14}$

$$0{\cdot}3108x-0{\cdot}9278y-0{\cdot}2065z=1{\cdot}5715$$

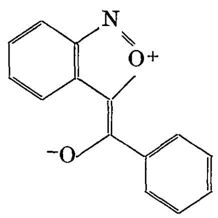
Atoms included		Atoms omitted	
C_9	0·006 Å	C_7	0·680 Å
C_{10}	−0·002	C_8	−0·018
C_{11}	0·001	O_2	−0·554
C_{12}	−0·004		
C_{13}	0·008		
C_{14}	−0·009		

In Table 5, the least square equations to the planes are given, together with the deviations from these planes.

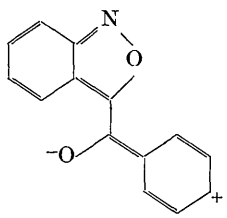
Although the anthranil ring system is very nearly coplanar throughout its nine atoms, there is some evidence that it might be slightly warped as judged by the deviations from planarity when the quinoid and isoxazole rings are considered separately. These results are consistent with a dihedral angle between the planes at the central C_1–C_6 bond of 1·6°, but this feature is only possibly significant.

The carbonyl group makes an angle of 8·2° with the anthranil plane, and the phenyl ring is twisted a further 30·5° from the carbonyl plane, so that the angle between the anthranil plane and the phenyl plane is 39°. As shown in Fig. 7, the anthranil and the phenyl planes are tilted in opposite directions with respect to the (010) plane, and it was for this reason that the molecule was thought to be planar from the results of the projection alone.

In so far as coplanarity is a measure of conjugation, it would appear therefore that the carbonyl group is more conjugated with the anthranil system than with the phenyl group. In terms of valence-bond diagrams, this corresponds with a greater weight for the Kekule type structures, IV, which have eight double bonds, as compared with structures such as V which have only seven double bonds.



IV



V

(*b*) *Bond lengths*

In the anthranil system, the benzene ring has an orthoquinoid arrangement of bonds, corresponding to the valence bond diagram II. However, the double bonds C_2–C_3, C_4–C_5 have an average length of 1·370 Å which is longer than a double bond, and the bonds C_1–C_2, C_3–C_4, C_5–C_6, C_6–C_1, with an average length of 1·415 Å, are significantly shorter than a single bond. If equal weight is given to one structure of type II and two of type IV, the shorter bonds have two thirds and the longer bonds have one third double bond character. Using Pauling's (1960) relationship, this gives, respectively, lengths of 1·371 and 1·423 Å, which are in good agreement with the observed values.

In the isoxazole ring, the C_1–N, O_1–C_7 and C_6–C_7 bonds are also intermediate in length between double and single bonds. The N–O distance, however, is 1·41 Å, which is greater than the sum of the usual single bond covalent radii. This must be a characteristic of this ring system, which has adjacent nitrogen and oxygen atoms with three pairs of unshared electrons between them. A similar N–O bond length of 1·41 Å has been reported in nitric acid by Maxwell & Mosley (1940).

The two acyclic C–C bonds, C_7–C_8 and C_8–C_9 differ in length by 0·05 Å. The geometry of the molecule, discussed in the previous section, would indicate that the greater resonance interaction was between the carbonyl group and the anthranil rings, and this in fact, corresponds with the shorter bond length of 1·473 Å. The phenyl group is inclined at 30° to the plane of the carbonyl valencies and the π bond interaction must be smaller, giving rise to the observed length of 1·520 Å. Dewar & Schmeising (1959) have suggested that 1·476 Å be the accepted length of a sp^2–sp^2 carbon σ bond with no π bonding and that many of the bond shortening effects previously ascribed to conjugation can be accounted for by differences in hybridization. It is difficult to account for these bond lengths in this way. As far as this molecule is concerned, the explanation that C_8–C_9 is a sp^2–sp^2 bond with very little π-bond character and that C_9–C_{10} is shorter by reason of a greater degree of π-bonding due to conjugation between the carbonyl group and the anthranil ring would seem to be most consistent with the molecular geometry. This would imply that the sp^2 carbon single-bond radius should be taken as at least 0·76 Å, i.e. longer than Dewar & Schmeising's (1959) suggested value and in closer agreement to Coulson's (1948) original suggestion.

The carbonyl C–O bond length is 1·22 Å, which is well within the range of normal observed values. The characteristic infra-red frequency is 90 cm.$^{-1}$ less than the normal value (Pinkus, Cohen, Sundaralingam & Jeffrey, 1960). While this may be a consequence of the conjugation or simply of the proximity to the adjacent isoxazole ring, there is no correspondingly abnormal stereochemical feature of the carbonyl group itself with which this spectroscopic observation can be associated.

Table 6. *Comparison of theoretical and experimental bond lengths*

Bond	Obs.	Calc.
C_1–C_2	1·39 Å	1·41 Å
C_2–C_3	1·36	1·38
C_3–C_4	1·43	1·40
C_4–C_5	1·38	1·38
C_5–C_6	1·42	1·41
C_6–C_1	1·43	1·42
C_6–C_7	1·39	1·42
C_7–C_8	1·47	1·42
C_1–N	1·34	1·36

A simple molecular orbital calculation was carried out for the anthranil ring system and the carbonyl group. The overlap integrals were assumed to be zero and the resonance integrals equal to β, irrespective of the atoms involved. The Coulombic integrals for the hetero-atoms were given the following usual values,

$$\alpha_N = \alpha + (x_N - x_C)\beta = \alpha + 0{\cdot}5\beta$$
$$\alpha_O = \alpha + (x_O - x_C)\beta = \alpha + 1{\cdot}1\beta$$

where x is the electronegativities of the atoms concerned. The calculated bond orders and electronic charges are shown in Fig. 6. The C–C bond distances were derived from the calculated bond orders using the order-length curve of Daudel, Lefebvre & Moser (1959). For the C–N bond a linear order-length curve was used with extreme values of 1·47 Å and 1·26 Å, the sum of the single and double bond covalent radii of carbon and nitrogen respectively. Table 6 illustrates the good agreement between the observed and calculated distances, only C_7–C_8 has a discrepancy greater than 0·03 Å. From Fig. 6 it is seen that an electrophilic substitution should preferentially take place at C_7.

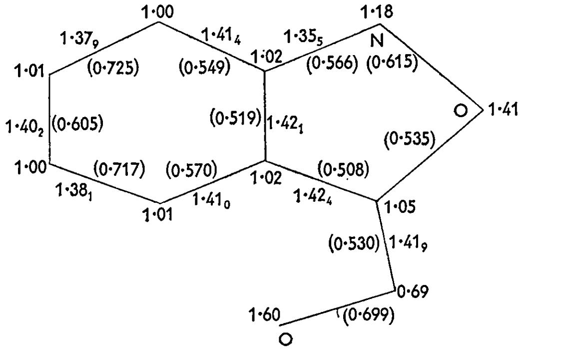


Fig. 6. Calculated bond orders, (in parenthesis), electronic charge and bond lengths in the anthraniloyl moeity.

The phenyl group is not regular, although the differences from the mean bond length of 1·393 Å do not exceed 0·03 Å and are barely significant. If, as suggested by Trotter (1960), we assume *mm*2 symmetry our results show the same trend as he discusses for other mono-substituted benzenes, i.e. a short, long, short, sequence for the 1–2, 2–3, and 3–4 benzene bonds.

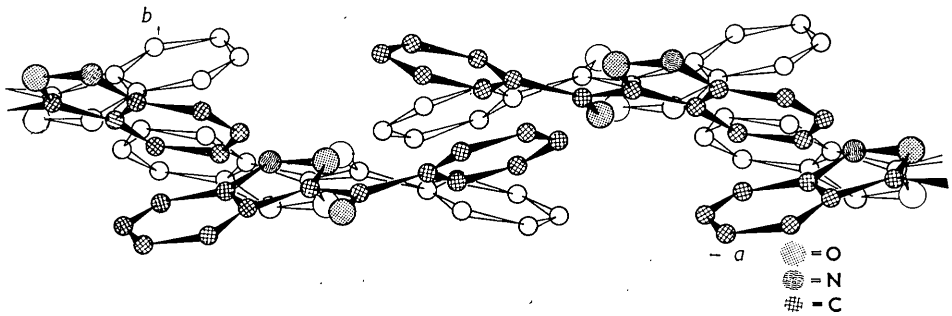


Fig. 7. Diagram showing molecular arrangement.

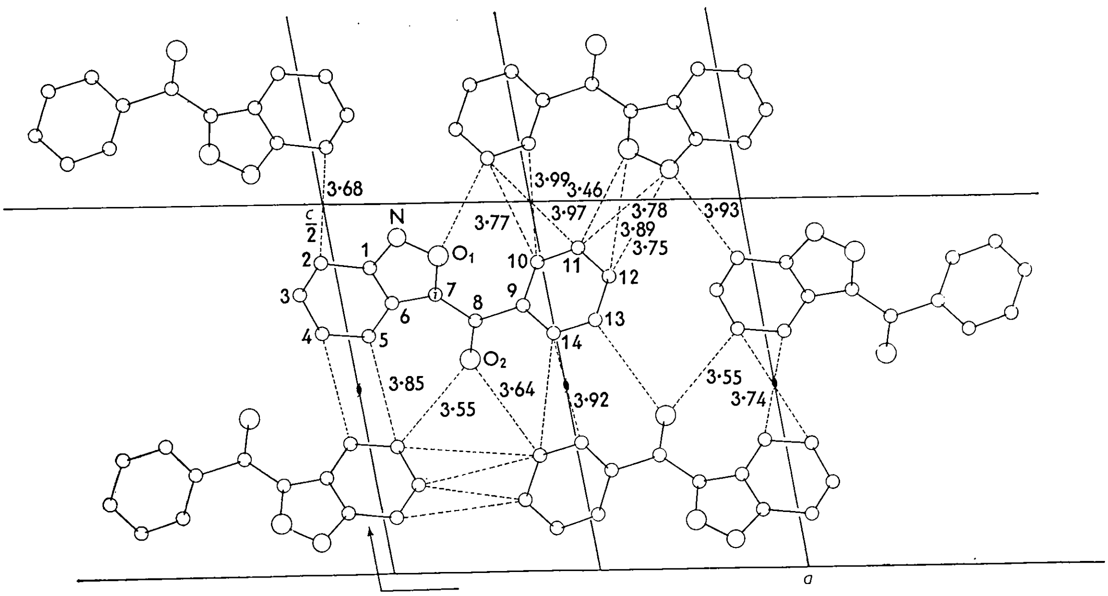


Fig. 8. Arrangement of molecules in (010) projection, showing the shorter intermolecular contacts (less than 4 Å).

(c) Intermolecular distances

All the intermolecular distances are greater than 3·4 Å, and the arrangement of the molecules with some of these distances is shown in Figs. 7 and 8.

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Short Communications

Contributions intended for publication under this heading should be expressly so marked; they should not exceed about 1000 *words; they should be forwarded in the usual way to the appropriate Co-editor; they will be published as speedily as possible. Publication will be quicker if the contributions are without illustrations.*

Acta Cryst. (1962). **15**, 1042

The unit cell and space group of Li_2C_2.

By D. R. SECRIST and L. G. WISNYI, *Knolls Atomic Power Laboratory,* U.S.A.*

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A review of the literature has indicated that no work has been reported on the unit cell or structure of the various alkali carbides.

As part of a study of the ternary system, lithium–boron–carbon, a brief examination of the lithium–carbon system was conducted. A single crystal of lithium carbide was synthesized and isolated for study. The crystal was formed by reacting lithium and graphite at 700 °C. for two days and slow-cooling. The elements were contained in an iron capsule with an argon atmosphere.

The crystal was identified as monoclinic. Weissenberg and rotation photographs were recorded about the b_0 axis. The Bradley–Jay (1932) extrapolation method was used to refine the a_0 and c_0 lattice constants computed from the zero-level Weissenberg photograph. The identity period along the b_0 axis was obtained from the rotation photograph. The angle β was measured directly on the zero-level Weissenberg photograph.

Debye–Scherrer X-ray powder patterns were made using nickel-filtered Cu $K\alpha$ radiation. Line intensities were visually estimated. The (hkl) combinations satisfying the powder pattern data were supplied by a computer. The observed and calculated $\sin^2\theta$ values are compared in Table 1. Since the identity period along the b_0 axis could only be measured to $\pm 0{\cdot}1$ Å, the b_0 value for each (hkl) reflection was recalculated using the a_0, c_0, and β measurements from the Weissenberg photograph and the corresponding observed $\sin^2\theta$ value from the powder pattern. In this manner, b_0 was refined to $\pm 0{\cdot}005$ Å. The resulting cell dimensions are:

$$a_0 = 7{\cdot}801 \pm 0{\cdot}002,\; b_0 = 8{\cdot}815 \pm 0{\cdot}005 \text{ Å},$$
$$c_0 = 10{\cdot}865 \pm 0{\cdot}005 \text{ Å};\; \beta = 76{\cdot}8 \pm 0{\cdot}1°.$$

The adjacent layer levels were similar and contained no systematic extinctions. The unit cell is, therefore, primitive and the space group is either $P2$, Pm, or $P2/m$. Since the crystal exhibited prismatic habit (elongated development along the c_0 axis), the space group $P2/m$ is suggested. The density of lithium carbide has been reported in the literature as 1·65 g.cm.$^{-3}$ (*International Critical Tables*, 1926). If the value is correct within 5%, the unit cell would contain 18 to 20 molecules. A chemical analysis of the carbide confirmed the 50–50 at.% combination. The formula ratio Li_2C_2 is discussed by Thorne & Roberts (1948), based on the production of acetylene when the alkali carbides react with water.

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