Acta Cryst. (1965). **18**, 5

The Crystal Structure of Triketoindane (Anhydrous Ninhydrin). A Structure Showing Close C=O···C Interactions

By William Bolton*

King's College, University of Durham, Newcastle-on-Tyne, England

(*Received* 7 *January* 1964)

Several recent crystal structure analyses have shown close approaches of about 2·8 Å between carbonyl carbon and oxygen atoms in different molecules. The C = O · · · C angles in each case are in the range 158 ± 4°. Perhaps the most interesting one is alloxan where the central carbon atom of the α, β, γ-triketo group is in close contact (2·79 Å) with two crystallographically equivalent α (or γ) oxygen atoms. There is no hydrogen bonding in the structure despite the presence of two > NH groups per molecule. The situation in alloxan and the other compounds with close C · · · O approaches was thought to be due to the presence of a greater charge than usual on the carbonyl carbon atom involved. It was thought that a similar situation would be found in triketoindane because of the inductive effects of O_α and O_γ. Two crystalline forms were discovered. An orthorhombic form with the space group *Pbca* and a tetragonal one which is $I4_1cd$.

The structure of the tetragonal form has been worked out. The molecule has implied twofold rotational symmetry and is planar within the limits of the analysis, and thus shows the full *mm* symmetry of the configurational formula in the crystal. The dimensions of the triketo group are almost identical with the alloxan values. In particular β CO is slightly short at 1·189 Å (1·186 Å in alloxan). This shortening may be due to induction of electrons from β C by the adjacent carbonyl group.

The intermolecular arrangement is such that β C is approached to within 2·83 Å from both sides of the molecular plane by α O and γ O in crystallographically equivalent positions. The C = O · · · C angle is 151°. This is a similar situation to the one in alloxan, as expected.

This latest example strengthens the conclusion that the close C · · · O approaches observed to date are real structural features with a common cause. This is considered to be the attraction for a charge centre $C^{\delta+}$ by the oxygen end of a $C^{\delta+} = O^{\delta-}$dipole. This attraction is large in these examples and manifests itself as a close approach although it may occur more generally in a weaker form in other compounds.

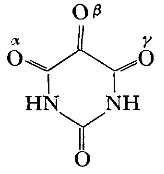
Introduction

Although numerous crystal structures of hydrogen-bonded organic compounds have been studied, there appear to be relatively few compounds in which, although the substance would normally crystallize as a hydrogen-bonded structure, as a hydrate for instance, care has been taken to examine the molecule in an environment with too few hydrogen atoms for complete hydrogen bonding of all electronegative atoms. One reason for this is that generally, if such compounds crystallize, they do so only with difficulty or decompose to a hydrate by reacting with atmospheric moisture. The author has examined four such proton-deficient compounds, and in three of them, namely anhydrous barbituric acid, alloxan and ninhydrin (Bolton, 1963, 1964*a* and this work) non-hydrogen-bonded carbonyl carbon and oxygen atoms are involved in close approaches. In parabanic acid (Davies & Blum, 1953) and chloranil (Chu, Jeffrey & Sakurai, 1963) there are similar close interactions. The O · · · C distances are about 2·8 Å and the associated C = O · · · C angles are all in the range 155° to 163°. In anhydrous alloxan (I) (Bolton, 1964*a*) where there are two > NH hydrogen atoms and four carbonyl oxygen atoms per molecule, the structure might be expected to be determined by the interplay of hydrogen bonding and van der Waals packing forces. It is without exception the case in structures of amides and imides so far reported that where the possibility of hydrogen bonding exists it is utilized in the actual crystal structure. However, in alloxan there is no hydrogen bonding at all, but the molecules are arranged so that the carbon atom of the central carbonyl group, C_β, is approached from both sides of the pyrimidine ring by O_α and O_γ in crystallographically equivalent positions at distances of 2·79 Å. It appears then that the C · · · O interactions associated with the close approaches mentioned above are predominant over possible hydrogen bonding in determining the structure of alloxan. The tentative explanation given for these interactions (Bolton, 1964*a*) is that in each case the carbon atom has a residual positive charge due to induction of electrons by electronegative ring substituents and is an electrostatic centre of attraction for the oxygen end of

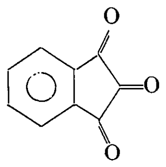
---

* Present address: Medical Research Council, Laboratory of Molecular Biology, Hills Road, Cambridge, England.

$C^{\delta+}=O^{\delta-}$ dipoles of adjacent molecules. If this is correct, the situation in alloxan would be due to a residual positive charge on the β keto carbon atom caused by the strong inductive effect of the α and γ CO groups. One might therefore expect a similar situation to occur in the crystal structures of other proton deficient α,β,γ-triketones, and it would be interesting to compare these with alloxan. There are no data of this kind available, and the structure of α,β,γ-triketoindane (II) has been examined to remedy this.

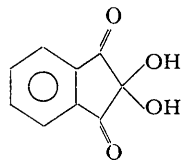


(I)



$C_9H_4O_3$

(II)



$C_9H_4O_3 \cdot H_2O$

(III)

Experimental

Triketoindane is obtained from water as the monohydrate (III), which is the reagent ninhydrin, widely used as a test for amino acids with free NH_2 groups. This substance is chemically very similar to alloxan monohydrate (Ruhemann, 1911) and crystals of the anhydrous substance were obtained in the same way as anhydrous alloxan, by slowly heating ninhydrin *in vacuo* below 90 °C to remove the chemically attached water, then subliming at 120 °C.

Two crystalline forms were obtained, and although (III) is colourless, both anhydrous forms were dark red in keeping with the presence of the strongly bathochromic triketo group in (II). The crystal data are:

Orthorhombic form:

$$a=15\cdot524\pm0\cdot008,\ b=14\cdot160\pm0\cdot008,$$
$$c=6\cdot380\pm0\cdot005\ \text{Å}\ .$$
$$D_m=1\cdot52,\ D_x=1\cdot526\ \text{g.cm}^{-3};\ Z=8\ .$$

Systematic absences $hk0$, $0kl$ and $h0l$ for h, k and l odd respectively give the space group uniquely as *Pbca*. Crystals of this form were present as small round pieces of indeterminate habit.

Tetragonal form:

$$a=7\cdot058\pm0\cdot005,\ c=28\cdot77\pm0\cdot01\ \text{Å}\ .$$
$$D_m=1\cdot48,\ D_x=1\cdot490\ \text{g.cm}^{-3};\ Z=8\ .$$

The systematic absences hkl for $h+k+l\neq2n$, hhl for $2h+l\neq4n$ and $0kl$ for $l\neq2n$, give the space group as $I4_1cd$. This form was obtained as long thin needles, acicular about c. The range of stability of the two polymorphs is not known; both forms were obtained together in all the sublimations.

The crystals decomposed to (III) immediately, on contact with water, and slowly in air. By coating with petroleum jelly it was possible to keep a single crystal unchanged for up to a week. Data have been collected for both modifications, but only the tetragonal one is described here. Intensities were recorded on $h0l$ to $h5l$ equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. This gave 380 of the possible 400 reflexions in the Cu $K\alpha$ sphere. These were eye-estimated and after reduction to structure amplitudes were placed on the same scale by internal correlation and by comparison with photographs taken with the crystal mounted about [110].

As there are 16 equivalent positions in the space group and 8 molecules in the unit cell, the molecule must have an implied twofold rotation axis of symmetry. This can only be the line AB in Fig. 1, through C(1), O(1) and the mid point of the bond C(5)C(5′). With this coincident with $x=y=0$ it is only necessary to find a single parameter, the angle (φ) between the molecular plane and the x or y axis, to solve the structure in principle, if the molecular configuration (II) is assumed *a priori*. It may be mentioned, to clarify this, that in this space group the origin of the unit cell can be chosen arbitrarily anywhere along $x=y=0$ and therefore a set of relative z coordinates based on (II) will be necessarily a good approximation to the correct ones. It was a simple matter to find φ by rotating the molecule, which projects as a line of atoms in the (001) projection (Fig. 1) within the volume allowed by packing considerations, and calculating $hk0$ structure factor agreement indices for each case. The lowest R value coincided with the best packing model and the x and y coordinates from this, together with z coordinates allocated on the basis of assumed bond lengths and angles, were used to calculate hkl structure factors. The first three-dimen-

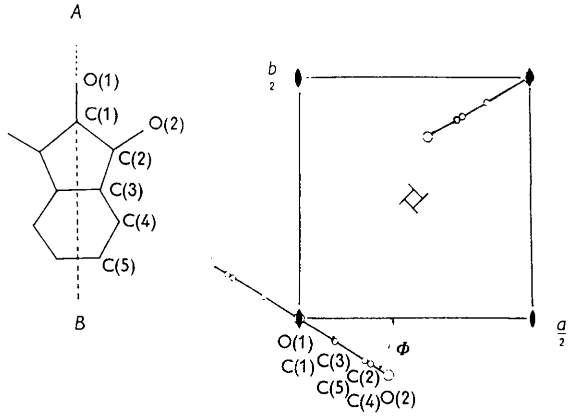


Fig. 1. Projection of the structure of triketoindane down the tetrad axis. The molecules lie with the axis AB coincident with the twofold rotation axis at $x=y=0$. Only the angle φ was required to solve the structure in principle.

sional calculation used all observed data and gave extremely good agreement with an R value of 14·5%. This was reduced further to 8·17% by several least-squares refinements using Cruickshank's (1957) program for the Ferranti Pegasus computer with Hughes's (1941) weighting scheme. Anisotropic temperature parameters were refined in the final cycles. The introduction of hydrogen atoms in fixed positions at 1·10 Å from the carbon atoms in the molecular plane, followed by a further cycle of least squares, reduced the R value to 7·87% and noticeably improved low order agreement. A final structure factor calculation, including non-systematically absent reflexions at half the threshold value, gave an R value of 9·3%. These reflexions are marked with an asterisk in Table 1 which gives the results of this calculation scaled up by 10.

The final atomic coordinates and their estimated

Table 1. *Observed and calculated structure factors*

	H	L	$\lvert F_o\rvert$	$\lvert F_c\rvert$
	0	4	979	1094
		8	1170	1245
		12	922	969
		16	848	885
		20	738	717
		24	664	661
		28	170	171
		32	141	111
		36	93	98
	2	0	986	982
		2	788	803
		4	659	705
		6	179	192
		8	886	920
		10	327	345
		12	640	625
		14	172	150
		16	143	131
		18	153	143
		20	217	137
		22	210	209
		24	544	516
		26	112	91
		28	160	137
		30	74	59
*		32	19	40
		34	19	30
	4	0	124	84
		2	205	237
		4	458	514
		6	143	154
		8	363	410
		10	432	416
		12	253	229
		14	122	95
		16	184	198
		18	134	139
		20	349	331
		22	134	137
		24	198	187
		26	115	97
		28	98	100
		30	67	59
		32	74	74
	6	0	91	81
		2	131	122
		4	294	319
		6	67	53
		8	181	168
		10	315	294
		12	191	203
		14	296	287
		16	110	115
		18	74	56
		20	124	124
		22	129	140
		24	72	73
		26	72	89
	8	0	91	75
*		2	19	40
		4	150	160
		6	88	66
		8	67	73
		10	57	45
		12	57	46
		14	69	68
		16	50	47
			K = 1	
	1	6	597	618
		10	740	698
		14	561	485
		18	215	191
		22	308	349
		26	397	411
		30	160	155
		34	76	64
	2	1	1003	935
		3	950	911
		5	256	335
		7	408	427
		9	432	455
		11	492	488
		13	224	230
		15	229	255
		17	170	169
		19	251	244
		21	165	167
		23	253	274
		25	117	129
*		27	24	32
		29	69	78
		31	86	98
*		33	24	25
	3	0	642	543
		2	616	658
		4	193	224
		6	334	331
		8	86	100
		10	380	376
		12	53	41
		14	420	425
		16	81	66
		18	220	193
		20	110	132
		22	196	195
		24	181	187
		26	64	58
*		28	24	33
*		30	24	34
*		32	24	46
		34	115	131
	4	1	322	312
		3	170	202
		5	287	302
		7	100	122
		9	174	160
		11	220	208
		13	198	190
		15	131	133
		17	160	172
*		19	24	22
		21	184	184
		23	162	162
		25	155	157
		27	96	97
*		29	24	44
		31	67	67
	5	0	107	86
		2	315	297
		4	53	38
		6	272	282
		8	160	152
		10	64	52
		12	296	296
		14	143	143
		16	174	150
		18	186	177
		20	72	47
		22	227	222
*		24	24	14
		26	100	84
*		28	24	45
	6	1	93	82
		3	122	122
		5	93	99
		7	122	147
		9	72	68
		11	72	77
		13	158	168
		15	67	83
*		17	24	50
*		19	24	50
*		21	23	25
	7	0	93	110
		2	131	210
		4	103	118
		6	103	114
		8	112	109
		10	62	77
		12	112	122
*		14	24	65
*		16	24	50
*		18	24	77
*		20	24	55
*	8	1	23	35
*		3	23	40
*		5	23	41
*		7	23	38
*		9	23	46
		11	69	53
			K = 2	
	2	0	1158	1212
		4	604	641
		8	105	75
		12	370	324
		16	406	391
		20	284	261
		24	208	178
		28	50	40
		32	93	75
	3	1	693	638
		3	232	247
		5	170	182
		7	64	59
		9	384	348
		11	186	175
		13	72	57
		15	141	141
		17	160	158
*		19	19	32
		21	265	240
		23	229	231
		25	191	193
		27	96	103
		29	50	57
*		31	19	39
	4	0	265	308
		2	377	365
		4	306	295
		6	141	148
		8	220	220
		10	107	98
		12	112	131
		14	170	160
		16	117	109
		18	110	94
		20	165	149
		22	124	135
		24	139	121
		26	72	64
		28	100	90
*		30	19	34
	5	1	334	327
		3	191	174
		5	72	67
		7	100	82
		9	201	206
		11	196	202
		13	119	97
		15	236	226
		17	81	86
		19	134	120
		21	96	105
		23	115	115
		25	136	120
*		27	19	44
*		29	19	8
	6	0	115	126
		2	105	123
		4	148	158
		6	105	98
		8	139	146
		10	139	144
		12	189	214
*		14	19	13
		16	96	100
*		18	19	45
		20	88	80
		22	76	84
		24	98	85
		26	69	64
*	7	1	19	27
		3	76	82
*		5	19	18
		7	57	60
		9	153	168
		11	179	182
		13	134	148
		15	38	90
*		17	19	28
*		19	19	46
	8	0	60	63
*		2	19	20
		4	115	142
*		6	19	27
*		8	19	42
*		10	19	25
*		12	19	51
			K = 3	
	3	2	165	147
		6	449	499
		10	322	288
		14	134	156
		18	220	219
		22	246	213
		26	210	201
		30	79	78
	4	1	306	316
		3	213	180
		5	124	109
		7	234	228
		9	155	124
		11	236	217
		13	427	388
		15	229	225
		17	98	90
		19	62	64
		21	139	137
		23	72	77
*		25	19	33
		27	79	76
		29	59	53
	5	0	232	194
		2	420	389
		4	172	176
		6	251	216
*		8	19	10
		10	263	229
		12	74	62
		14	131	124
		16	64	71
		18	143	140
		20	74	79
		22	53	43
		24	179	160
		26	91	74
	6	1	110	90
		3	134	134
		5	69	62
		7	112	109
		9	60	62
		11	129	121
		13	107	122
*		15	19	55
		17	53	52
*		19	19	13
		21	45	57
		23	72	89
	7	0	215	221
		2	110	143
		4	91	85
		6	62	90
		8	107	118
		10	50	57
		12	72	79
*		14	19	53
*		16	49	74
*	8	1	19	39
*		3	19	45
		5	50	56
		7	55	57
		9	57	72
		11	76	93
			K = 4	
	4	0	298	342
		4	215	226
		8	105	99
		12	177	185
*		16	19	51
		20	60	50
		24	105	101
		28	105	97
	5	1	143	141
		3	112	107
		5	146	147
		7	136	137
		9	232	222
		11	227	218
		13	158	141
		15	55	40
		17	55	55
		19	53	43
		21	48	40
		23	70	53
		25	84	90
	6	0	115	125
		2	191	209
		4	160	165
		6	96	86
*		8	19	32
		10	112	115
*		12	19	7
		14	110	89
		16	60	55
		18	74	69
		20	74	86
	7	1	119	130
		3	88	99
*		5	19	29
		7	57	56
		9	57	54
		11	57	55
		13	103	99
	8	0	88	120
*		2	19	28
			K = 5	
	5	2	153	163
		6	76	67
		10	141	144
		14	81	80
		18	72	48
		22	124	130
	6	1	103	106
		3	41	23
		5	48	39
		7	50	33
		9	60	52
		11	81	57
*		13	19	39
*		15	19	21
*		17	19	53
*		19	19	44
	7	0	36	21
		2	55	65
		4	38	34
		6	45	55
		8	41	53
		10	64	86

standard deviations are given in Table 2. The anisotropic thermal parameters shown alongside have $\sigma(B_{ii})=0{\cdot}22$ Å^2 and $\sigma(B_{ij})=0{\cdot}40$ Å^2.

Table 2. *Atomic coordinates* (Å) *and temperature parameters* (Å^2)

	x	y	z	e.s.d.
C(1)	0	0	2·2577	0·0090
C(2)	1·0532	0·6011	1·3301	0·0067
C(3)	0·6057	0·3426	−0·0534	0·0062
C(4)	1·2381	0·6766	−1·2467	0·0067
C(5)	0·6167	0·3453	−2·4200	0·0068
O(1)	0	0	3·4447	0·0075
O(2)	2·0722	1·1656	1·7130	0·0060
H(1)	1·120	0·585	−3·370	—
H(2)	2·190	1·200	1·245	—

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
C(2)	3·74	2·25	3·14	−0·04	0·45	−0·87
C(3)	3·20	2·34	2·74	0·07	−0·36	−0·09
C(4)	3·11	3·21	2·97	−0·48	1·30	0·39
C(5)	3·68	4·55	2·70	1·70	1·08	0·97
O(2)	5·02	4·87	4·09	−5·55	1·06	−3·00

Isotropic: $B(\mathrm{C}(1))=2{\cdot}87$, $B(\mathrm{O}(1))=3{\cdot}44$ Å^2.

Discussion

The triketoindane molecule

The molecular dimensions are shown in Fig. 2. The molecule has a twofold axis of symmetry passing through the β keto bond C(1)O(1) and is planar within the limits of the determination. The equation for the molecular plane is $0{\cdot}4891x-0{\cdot}8722y=0$. The deviations from this are C(2) $=-0{\cdot}010$, C(3) $=-0{\cdot}003$, C(4) $=0{\cdot}015$, and C(5) $=0$ and O(2) $=-0{\cdot}004$ Å. In the crystal the molecule thus shows the full *mm* symmetry of its configurational formula.

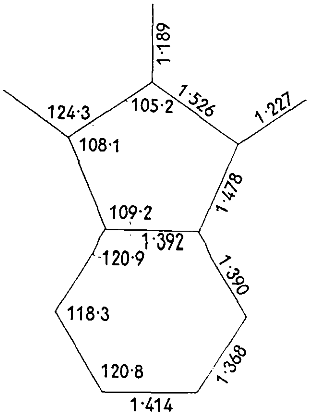
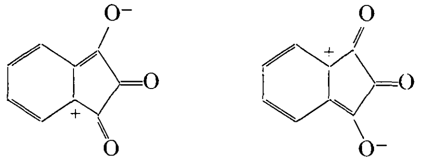


Fig. 2. The dimensions of the triketoindane molecule.

None of the CC bond lengths show highly significant differences from the values of 1·397 and 1·504 Å (Pauling, 1960) to be expected from the configurational formula; however, the differences that do exist are systematic, and consistent with resonance contributions of a total of about 7% from the charged forms:



The dimensions of the triketo group here are very similar to those in alloxan, thus β CO $=1{\cdot}189$ Å (1·186 in alloxan), α CO $=1{\cdot}227$ Å (1·213) and $\alpha\beta$ CC $=1{\cdot}526$ Å (1·521). It is particularly interesting that β CO is in both cases less than the usual C=O distance of 1·21 Å, as it is not possible to account for the shortening without postulating resonance contributions from structures with no bonds between C_β and C_α or C_γ. A possible explanation is that the induction of electrons away from C_β by the α and γ carbonyl groups leaves a slight residual positive charge on C_β which approaches more closely to O_β by electrostatic attraction. Another way of saying this is that a residual positive charge on C_β will reduce the electronegativity of this atom and consequently increase the Schomaker & Stevenson (1941) C=O bond length correction term. It can easily be deduced that if this is correct the difference in electronegativity of C_β and O_β compatible with a CO bond length of 1·187 Å is about 1·25, an increase of 0·25 over the difference corresponding to the usual value of 1·21 Å. This of course is a very tentative conclusion and because of the small differences in bond length concerned may be quite wrong. However, a positive charge on C_β is compatible with the role of this atom in the intermolecular structure (see introduction and below).

The intermolecular structure

An isometric drawing of the structure is shown in Fig. 3. At the same z level molecules are packed with their symmetry axes parallel to **c**. The resulting sheets of molecules are $c/4$ thick and are stacked parallel to (001), one above the other in a closest-packing arrangement. The intermolecular contacts (Table 3) between molecules in different sheets are all greater than the sum of the van der Waals radii. However, within a sheet (Fig. 3) each molecule has close links to its four nearest neighbours. These are through the α and γ carbonyl oxygen atoms and close approaches at C_β (O(2), O(2′) and C(1) respectively in Fig. 4) from both sides of the molecular plane. They link the molecules into a two-dimensional diamond mesh pattern (Fig. 4). These interactions are crystallographically equivalent and are 2·85 Å

Table 3. *The intermolecular distances less than* 4·0 Å

C(1)(I)–H(1)(V)	3·52 Å
C(1)(I)–H(1)(VII)	2·93
C(1)(II)–O(2)(I)	2·83
C(1)(II)–C(2)(I)	3·95
C(1)(I)–C(5)(VII)	3·86
C(2)(II)–C(2)(I)	3·81
C(2)(II)–O(2)(I)	3·02
C(2)(III)–O(2)(I)	3·10
C(2)(I)–H(2)(V)	3·57
C(2)(II)–H(2)(I)	2·95
C(2)(III)–H(2)(I)	2·95
C(2)(I)–H(1)(VII)	3·12
C(3)(II)–C(4)(I)	3·80
C(3)(II)–O(2)(I)	3·34
C(3)(III)–O(2)(I)	3·39
C(3)(II)–H(2)(I)	3·06
C(3)(III)–H(2)(I)	3·07
C(4)(I)–C(4)(II)	3·68
C(4)(VII)–O(1)(I)	3·46
C(4)(II)–H(2)(I)	3·90
C(4)(III)–H(2)(I)	3·95
C(4)(I)–C(5)(II)	3·80
C(5)(I)–O(1)(VIII)	3·22
C(5)(I)–O(2)(IX)	3·71
C(5)(VII)–O(1)(I)	3·22
C(5)(V)–O(1)(I)	3·50
C(5)(II)–H(1)(I)	3·86
C(5)(VI)–O(2)(IX)	3·59
O(1)(I)–H(1)(V)	3·17
O(1)(I)–H(1)(VII)	2·51
O(1)(II)–O(2)(I)	3·27
O(2)(I)–O(2)(II)	3·58
O(2)(I)–O(2)(III)	3·73
O(2)(I)—H(1)(V)	3·23
O(2)(I)–H(1)(VII)	2·87
O(2)(II)–H(2)(I)	3·60
O(2)(III)–H(2)(I)	3·64
O(2)(IV)–H(2)(I)	3·60
O(2)(IX)–H(1)(VI)	2·94

(I)	x, y, z	(VI)	$\bar{x}, \bar{y}, z$
(II)	$\frac{1}{2}-x, \frac{1}{2}+y, z$	(VII)	$y, \frac{1}{2}-x, \frac{1}{4}+z$
(III)	$\frac{1}{2}+x, \frac{1}{2}-y, z$	(VIII)	$\frac{1}{2}-y, x, -\frac{1}{4}+z$
(IV)	$1-x, -y, z$	(IX)	$-y, \frac{1}{2}-x, -\frac{1}{4}+z$
(V)	$\frac{1}{2}-y, -x, \frac{1}{4}+z$		

(the normal C · · · O distance is about 3·1 Å, Pauling, 1960) with a C=O · · · C angle of 151°, which is similar to the values previously found (Bolton, 1964*a*, Table 4 where the mean values are 2·82 Å and 158°).

There is a close resemblance here to the situation in alloxan (see introduction), and Fig. 5 shows the arrangement of close C=O interactions for each molecule, for comparison. In particular it seems that a *β*-keto carbon interaction with *α*(*γ*) oxygen atoms, from both sides of the molecular plane, is an important factor in deciding the arrangement in the crystal. On the basis of simple hydrogen bonding and packing considerations a close similarity between the two structures would not be expected. However the factor in common between the two was forecast, or at least expected, by considerations of an until recently unknown structural feature, namely a close C · · · O interaction associated with certain proton deficient structures (Bolton, 1964*a*). This strengthens the author's conclusion that the close approaches in the substances mentioned in the introduction are real

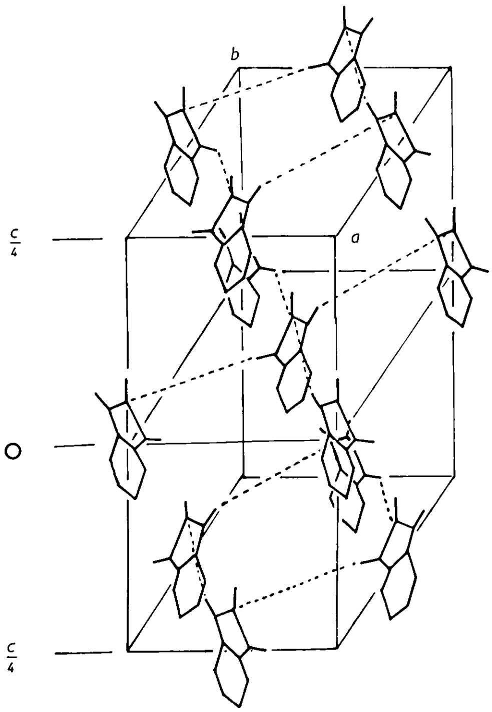


Fig. 3. An isometric drawing of the structure of triketoindane. The dotted lines show close C(1) · · · O(2) approaches. The molecules are not drawn to scale.

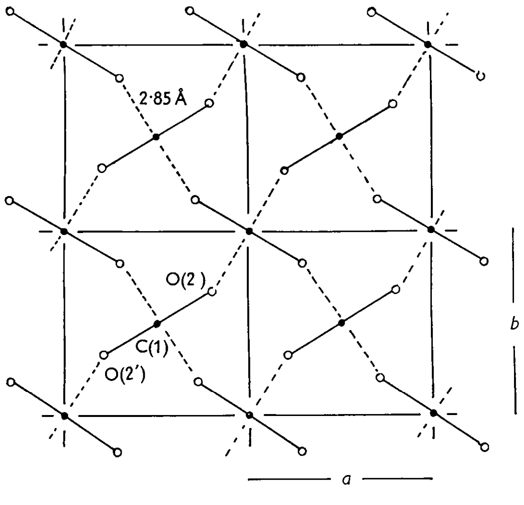


Fig. 4. A bounded projection of the structure of triketoindane of thickness *c*/4. The dotted lines show how the carbon–oxygen close approaches link a molecule to its four nearest neighbours at the same level of *z*. Only C(1) and O(2) are shown.

structural features with a common cause and that carbonyl carbon–oxygen interaction can in some cases (*e.g.* alloxan and triketoindane) be an important structural determinant.*

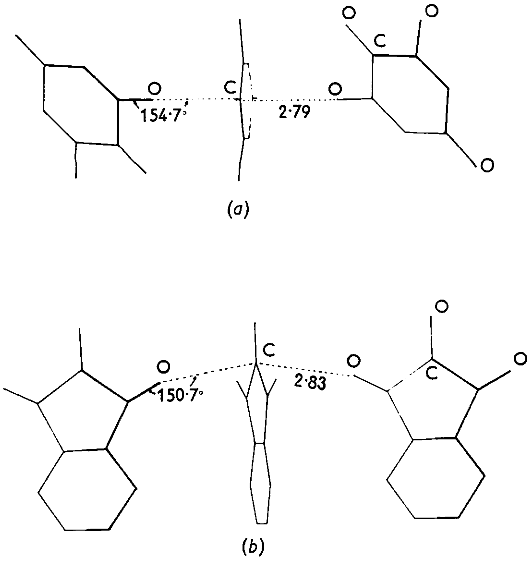


Fig. 5. The close $C\cdots O$ approaches in (*a*) alloxan and (*b*) triketoindane. In each case the molecules lie on a twofold rotation axis and the central atom of the triketo group is approached from opposite sides of the molecular plane by oxygen atoms in crystallographically equivalent positions.

This new example of a close $C\cdots O$ interaction can be explained (as can the other examples; Bolton, 1964) by assuming that because of the powerful inductive effect on C_β by the α and γ carbonyl groups there are stronger than usual attractive forces between $C^{\delta+}=O^{\delta-}$ dipoles, and the charge centre $\beta\ C^{\delta+}$ in different molecules, which are able to bring carbonyl atoms closer together than London dispersion forces allow. On the basis of this simple description the $C=O\cdots C$ angle will be expected to approach towards 180°, as the attraction of a dipole is strongest along its axis. In this respect the observed value of 151° is in poorer agreement than the earlier examples and shows the weaknesses of this kind of qualitative explanation which ignores the effect of other intermolecular packing requirements. It does not, however, destroy the conclusion that the close $C\cdots O$ approaches are due to electrostatic attraction between carbon and oxygen atoms.

It might be mentioned in conclusion that Kihara (1963) has recently arrived at the correct structures for some molecular crystals by assuming that they are governed by electrostatic forces between molecules. If this is correct, then the close $C\cdots O$ approaches observed to date may be just rather stronger examples of a more widespread structure determining factor.

References

Bolton, W. (1963). *Acta Cryst.* **16**, 166.
Bolton, W. (1964*a*). *Acta Cryst.* **17**, 147.
Bolton, W. (1964*b*). *Nature, Lond.* **201**, 987.
Chu, S. C., Jeffrey, G. A. & Sakurai, T. (1963). *Acta Cryst.* **15**, 661.
Cruickshank, D. W. (1957). Private communication.
Davies, D. R. & Blum, J. J. (1955). *Acta Cryst.* **8**, 129.
Hughes, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
Kihara, T. (1963). *Acta Cryst.* **16**, 1119.
Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.
Ruhemann, S. (1911). *J. Chem. Soc.* **99**, 793, 1486.
Schomaker, V. & Stevenson, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37.

---

* This effect is discussed in detail elsewhere (Bolton, 1964*b*).