The Structure of Overcrowded Aromatic Compounds. Part II.* The Crystal Structure of Dianthronylidene.

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The crystal structure of dianthronylidene (dianthrone) has been analysed by two-dimensional Fourier methods. The molecular centre being fixed by space-group symmetry, the molecular orientation and the signs of approximately half the $h0l$ structure factors were determined by the method of the molecular Fourier transform, calculated for a planar molecular model. The three zonal projections were refined by successive $F_O - F_C$ syntheses to R factors of 0·19, 0·19, and 0·20 in the $h0l$, $hk0$, and $0kl$ zones.

A molecular model has been obtained, approximating to symmetry $2/m$, in which a centre-to-centre distance of 2·90 Å between the overcrowded carbon atoms 4 and 4′, and 8 and 8′, is achieved by a 40° rotation of the benzene rings out of the plane of the central ethylenic system; this rotation is accompanied by compression of the $\underset{C}{\overset{C}{\diagdown}}C=$ angle to 113° and by deflection of the exocyclic bonds to the carbonyl carbon by 8° out of the planes of their respective benzene rings. The observed bond lengths and angles indicate that the molecule consists of an isolated ethylenic group (1·31 Å) attached by single bonds (1·53 Å) to normal benzene rings, which are linked in turn to a carbonyl group (1·20 Å) by single bonds (1·52 Å).

The absence of abnormally-short intermolecular contact distances in the crystal lattice indicates that the present molecular model may be identified with the ground state of dianthronylidene.

THE crystal structure of dianthronylidene (Fig. 1) † was determined in connection with a general investigation outlined in Part I.* The immediate purpose of this study was to determine the molecular shape of dianthronylidene with particular reference to the distance between the carbon atoms 4 and 4′ and 8 and 8′. The present paper reports the results of a structure analysis by two-dimensional Fourier methods and discusses the mechanism of relief of overcrowding.

Table 1 lists the crystallographic constants of dianthronylidene and of those of its derivatives that were available at the start of this work. For the purpose of an X-ray crystallo-

TABLE 1. *Crystallographic constants of dianthronylidene and some derivatives.*

	a	b	c	β	Space-group	d calc.	d exp.	n	Mol. sym.
Dianthronylidene	10·20	8·45	12·67	119° 48′	$P2_1/c$	1·345	1·35	2	$\bar{1}$
4 : 4′-Dibromo-	10·31	27·76	7·66	102° 30′	$P2_1/n$	1·675	1·695	4	—
4 : 4′-Dimethyl-	9·99	27·35	7·66	92° 22′	$P2_1/n$	1·307	1·320	4	—
3 : 4-3′ : 4′-Dibenzo-	14·7	11·5	7·6	α, 103° β, 92° γ, 101°	$P1$ or $P\bar{1}$	1·326	1·33	2	—

graphic analysis, only dianthronylidene itself and the isomorphous pair, 4 : 4′-dibromo- and 4 : 4′-dimethyl-dianthronylidene, seemed promising, the other derivative being too complex. Since so far we have not been able to grow entirely satisfactory crystals of the dibromo-compound, work was begun on dianthronylidene. From the lattice parameters of the crystals and their density, measured by flotation in a solution of potassium mercuri-iodide, it follows that there are two molecules in the unit cell. Hence, each molecule must possess a centre of symmetry, which may be placed at the points (000) and (0½½), and the problem of the structure analysis reduces to the determination of the (xyz) co-ordinates of 15 atoms, the hydrogen atoms being neglected.

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* Part I, preceding paper.

† In this paper the numbers used in references to the carbon atoms are as shown in Fig. 1 and not those strictly related to the name dianthronylidene.

Experience gained with the molecular Fourier transform method in the early stages of structure analysis suggested the use of the method in this instance. Apart from the limitations discussed below, we may say that the structure was solved by means of the Fourier transform. The simple form, as first applied to structure analysis by Knott (*Proc. Phys. Soc.*, 1940, **52**, 229) and later elaborated by Klug (*Acta Cryst.*, 1950, **3**, 176) (see also Herbstein and Schmidt, *Bull. Res. Council, Israel*, 1951, **1**, 123), strictly applies only to planar molecules, for which the Fourier transform is a function of the co-ordinates in the molecular plane only and can therefore be readily calculated as a two-dimensional series. In general, it consists of a real and an imaginary part, the latter vanishing for centrosymmetric molecules. Although dianthronylidene is in fact centrosymmetric, it cannot *a priori* be assumed planar, and hence the simple form of the Fourier transform method may not be applicable. Nevertheless, one could envisage the possibility that, calculated on the simplifying assumption of a planar molecule, it might give a sufficiently good first approximation, at least in one zone; the necessary condition would be that the projected view of the real molecule should not deviate markedly from the projection of the fully planar model. That this condition would be fulfilled for the $h0l$ zone was indicated by the relatively short b axis in dianthronylidene, and the still shorter c axis in 4 : 4'-dibromodianthronylidene; it appeared that the molecules in each compound were packed in a two-layer structure along the short axis, rather than at the steep angle to this axis required by the estimated molecular dimensions.
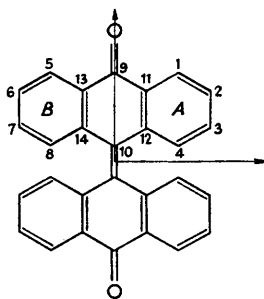

FIG. 1. *The planar model of the dianthronylidene molecule, showing the molecular axes and the nomenclature of the atoms used in this paper.*

The molecular Fourier transform of dianthronylidene was therefore calculated on the assumption of a planar model containing regular benzene rings of side 1·40 Å; in order to maintain periodicity, and hence to facilitate computation, the central C=C bond and the C=O bond were also assigned lengths of 1·40 Å. The contributions of the oxygen and carbon atoms were weighted in the ratio 8 : 6.

The map of the Fourier transform was compared with the plot of the weighted reciprocal lattice in the usual way, and the molecular axes were adjusted with respect to the reciprocal axes until fair agreement was obtained between observed and calculated structure factors. It was found that *three* orientations, at 120° to one another, gave roughly equal agreement for structure factors up to 2 sin θ = 1·5. The explanation for the indeterminacy in the Fourier transform method lies primarily in the approximate sixfold symmetry in the distribution of the areas of heavy scattering in the Fourier transform of dianthronylidene and in the uncertainty of the finer detail outside these areas. The three Fourier projections on to (010), each calculated from about 45 terms, including most of the strong reflections,

TABLE 2.—*Values of the agreement factor R for* F(h0l) *up to* 2 sin θ = 1·0, *showing the progress of refinement of the atomic co-ordinates derived from* ρ$_I$, ρ$_{II}$, *and* ρ$_{III}$.

Orientn. no.	Refinement no.			Orientn. no.	Refinement no.			Orientn. no.	Refinement no.		
	1	2	3		1	2	3		1	2	3
I	46	42	40	II	45	48	—	III	40	37	33

to which phase angles could be assigned from the corresponding Fourier transform orientation, were refined successively until a selection among them could be made on the basis of the relative improvement of the agreement factors. Table 2 shows the R factors, for F(*h0l*) up to 2 sin θ = 1·0, for the initial structure and after one and two stages of refinement. Orientation III was found to improve faster than I or II and was therefore chosen

as likely to lead to the correct structure. Further refinement was made by the use of the $F_O - F_C$ synthesis. The final Fourier projection on to (010) is shown in Fig. 2; it is clear at this stage that the molecule is not planar.

The projected view of the molecule is consistent with several more or less plausible models; structure factors $F(hk0)$ and $F(0kl)$ were computed for these possibilities up to $2 \sin \theta = 0.7$, and that model was chosen for which the R factor was lowest. Refinement of both zones was again carried out by the $F_O - F_O$ method; owing to the very heavy overlap, which affects different groups of atoms in the two projections, the two zones were refined alternately, with the y co-ordinates from one zone as the starting point in the second, and *vice versa*. The final y co-ordinates are the result of the minimisation technique

FIG. 2. *The electron-density projection on* (010). *The contours are drawn at intervals of* 1 e.Å^{-2}; *the lowest contour is the one-electron line.*
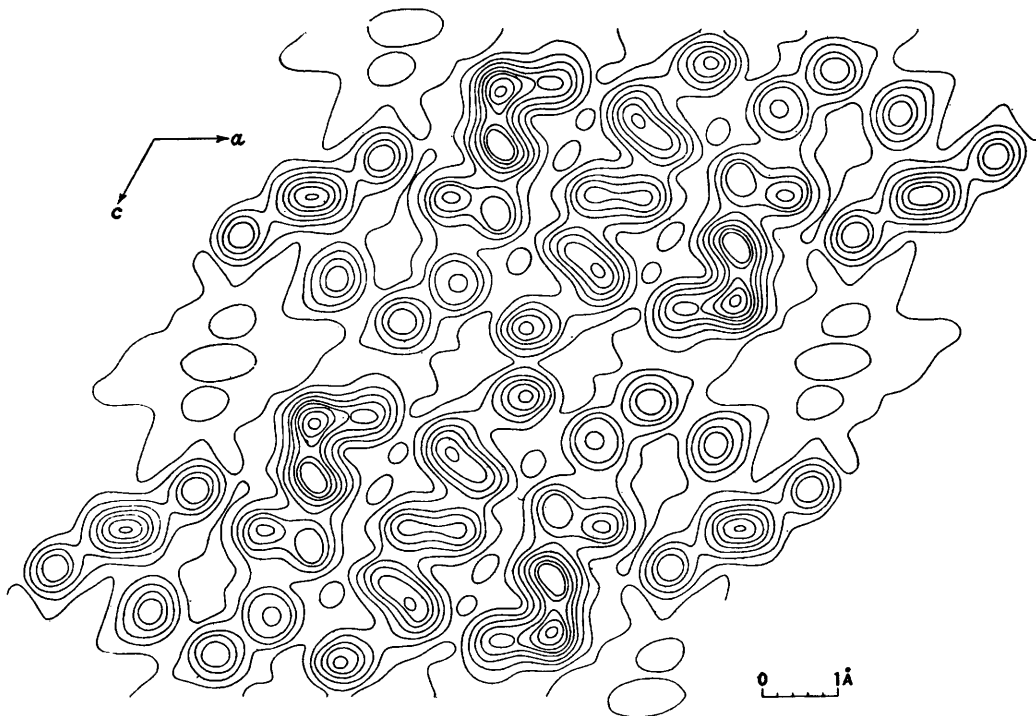

TABLE 3.—*Experimentally-measured atomic co-ordinates* (*in* Å).

Atom *	x	y	z	Atom *	x	y	z	Atom *	x	y	z
1	4·28	1·28	3·92	6	−1·83	0·34	3·53	11	2·81	0·72	3·09
2	4·86	2·07	3·22	7	−2·73	0·64	1·94	12	1·89	0·92	1·51
3	3·96	2·33	1·61	8	−2·08	0·57	1·05	13	0·40	0·00	3·21
4	2·38	1·77	0·75	9	2·17	−0·06	3·93	14	−0·53	0·28	1·62
5	−0·22	0·06	4·19	10	0·27	0·33	0·65	O	2·95	−0·44	5·23

* See footnote, p. 3295.

without extraneous assumptions on molecular dimensions. Although the x and z co-ordinates from the $h0l$ zones were used in the calculation of the first set of $hk0$ and $0kl$ structure factors, these co-ordinates were changed during the course of refinement of the two projections. The values resulting from this refinement were averaged with those originally obtained from the $h0l$ zone to give the final x and z co-ordinates listed in Table 3; the observed and calculated structure factors are compared in Table 4. Final R factors

TABLE 4.—*List of observed and calculated structure factors.*

hkl	F_O	F_C	hkl	F_O	F_C	hkl	F_O	F_C	hkl	F_O	F_C
002	44	−59	30$\bar{4}$	11	− 8	060	6	− 6	470	0	− 3
4	16	−13	4	4	1 *	8	5	1 *	5	0	1
6	31	−26	5	6	8	10	2	− 1	6	3	0 *
8	0	4	6	11	16				7	2	6
10	6	− 9	7	8	− 8	110	31	−28	8	0	1
12	5	4	8	0	− 2	2	24	−23			
14	6	− 4	9	8	8	3	20	−17	180	0	1
			10	5	4	4	25	21	2	9	13
100	34	40	11	4	− 5	5	9	− 8	3	6	− 2 *
2	32	−28				6	2	− 4	4	0	− 1
3	11	8	10$\bar{6}$			7	3	2	5	6	5
4	54	55	2	24	33	8	0	1	6	4	4
5	36	29	3	4	− 3	9	4	− 3	7	0	− 4
6	5	− 3	4	13	− 9	10	2	0 *			
7	3	2	5	28	29				190	0	3
8	7	− 6	6	10	− 9	120	69	85	2	0	4
9	11	−10	7	10	12	2	14	−13	3	5	− 3
			8	12	12	3	32	26	4	4	3
102	27	29	9	18	17	4	36	33			
2	24	−20	10	3	− 2	5	10	10	1,10,0	4	6
3	7	− 7	11	4	− 5	6	10	9	2	8	− 3 *
4	5	3	12	5	8	7	5	5			
5	12	13				8	11	−10	011	17	22
6	7	−11	10$\bar{8}$	0	− 1	9	6	− 5	2	37	−48
			2	5	6	10	0	0	3	22	26
104	10	−11	3	0	6				4	28	−28
2	15	17	4	0	0	130	38	36	5	25	−32
3	12	−11	5	6	− 7	2	10	− 5	6	14	14
4	15	14	6	10	10	3	10	− 8	7	16	14
5	19	−17	7	0	2	4	3	− 5	8	2	− 2
6	11	− 1*	8	0	− 1	5	9	9	9	0	− 2
7	7	6	9	17	−21	6	0	2	10	0	− 2
8	3	4	10	3	4	7	0	− 1	11	13	−10
			11	10	14	8	8	− 4	12	5	4
106	0	− 1	12	4	− 4	9	4	1 *	13	1	0 *
2	0	− 1	13	3	− 6	10	3	− 4			
3	4	10							021	42	−55
4	23	−20	10,$\bar{10}$	8	10	140	24	20	2	22	−21
5	3	− 2	2	13	−12	2	24	23	3	0	− 1
6	0	− 2	3	20	−20	3	14	11	4	8	− 6
7	4	− 2	4	31	−33	4	16	16	5	3	− 3
			5	5	− 3	5	8	8	6	4	− 3
108	5	− 3	6	0	0	6	6	6	7	2	0 *
2	8	8	7	0	− 4	7	8	− 7	8	7	− 4
3	0	− 1	8	10	− 9	8	5	3	9	4	− 4
4	8	− 6	9	7	− 8	9	0	0	10	0	1
5	10	− 9	10	0	1	10	3	− 1 *	11	0	2
6	0	0	11	3	5				12	5	5
7	2	− 3	12	5	5	150	18	23	13	2	2
						2	4	7			
10,10	18	−16	10,$\bar{12}$	8	− 8	3	8	− 9	031	10	− 4 *
2	5	− 4	2	3	− 2	4	0	− 3	2	31	−30
3	0	0	3	8	5	5	0	2	3	10	8
4	0	0	4	18	19	6	0	1	4	16	−13
5	5	6	5	14	−13	7	0	2	5	7	− 7
			6	4	− 4	8	5	5	6	10	9
10,12	5	4	7	5	7	9	8	11	7	10	8
2	5	− 2	8	3	2				8	5	3
			9	3	3	160	14	16	9	0	1
10$\bar{2}$	11	−12				2	17	20	10	0	2
2	16	−12	10,$\bar{14}$	5	− 5	3	6	7	11	6	− 4
3	32	33	2	4	− 4	4	3	− 3	12	2	1
4	25	−26	3	4	3	5	11	10	13	3	− 3
5	22	−22	4	5	− 4	6	0	1			
6	16	15				7	0	− 1	041	24	−23
7	4	− 1*	60,$\bar{16}$	5	− 7	8	2	− 3	2	14	−14
8	3	4	7	7	− 8	9	5	6	3	4	0 *
9	11	15	8	3	− 4				4	10	8
						170	11	14	5	4	5
10$\bar{4}$	0	1	020	63	80	2	3	4	6	4	− 6
2	10	15	4	35	41	3	0	− 3	7	8	7

TABLE 4. (*Continued.*)

hkl	F_O	F_C	hkl	F_O	F_C	hkl	F_O	F_C	hkl	F_O	F_C
048	4	1 *	059	6	— 3	071	10	— 8	086	3	4
9	11	—11	10	4	6	2	0	— 2	7	4	— 3
10	8	— 6	11	2	— 2	3	9	8	8	2	4
11	0	1	12	3	— 1	4	10	— 9	9	2	— 1
12	2	2				5	10	— 8			
13	2	3	061	4	— 3	6	0	— 1	091	0	— 1
			2	7	— 6	7	6	4	2	0	3
			3	4	1 *	8	4	— 1 *	3	5	3
051	12	— 9	4	6	5	9	6	8	4	3	— 3
2	28	—30	5	9	— 9	10	4	4	5	2	— 2
3	23	25	6	12	12				6	2	3
4	10	—11	7	6	— 5	081	0	— 2			
5	5	— 5	8	11	— 9	2	10	—10	0,10,1	0	1
6	0	2	9	4	— 3	3	2	1	2	2	— 2
7	0	— 4	10	3	4	4	4	4	3	2	— 1
8	0	— 1	11	6	5	5	4	4	4	2	0 *

FIG. 3. *The electron-density projection down* [100]. *Contours below the three-electron line have been omitted.*
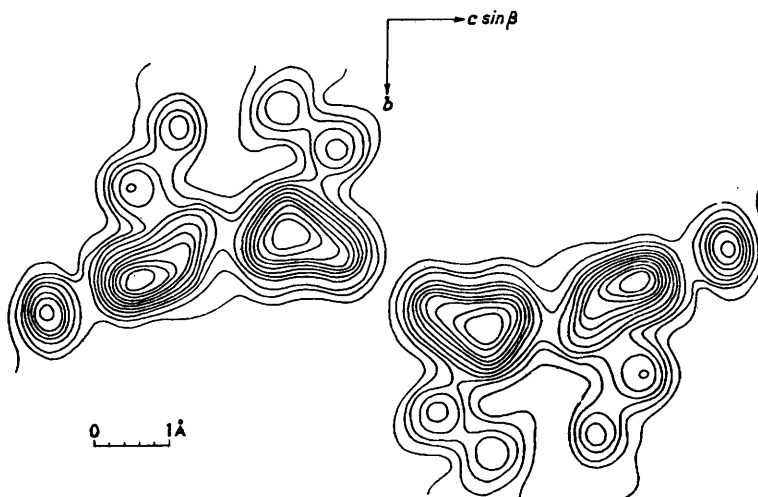
are 0·19, 0·19, and 0·20 in the *h*0*l*, *hk*0, and 0*kl* zones respectively. Fig. 3 shows the electron-density projection down [100].

Because of the considerable overlap in all three zones, the error in the final atomic co-ordinates is probably not less than 0·02 Å in *x* and *z*, though it may be somewhat smaller for the well-resolved atoms, and 0·05 Å in *y*. One can form an estimate of the former figure from the results of the F_O — F_C syntheses in the *hk*0 and 0*kl* zones, for which the final co-ordinates differ by a maximum of 0·05 Å and a mean of 0·03 Å from those of the *h*0*l* zone. A second estimate can be based on the internal consistency of the molecular dimensions. Comparison of chemically-equivalent bond lengths (Fig. 7) shows an average deviation of 0·02 Å, with a maximum deviation of 0·06 Å, from the mean. A similar analysis of equivalent bond angles shows an average deviation of 1° and a maximum deviation of 3° from the mean. Within the estimated limits of error, the molecule has the chemically-reasonable symmetry 2/*m*.

The following discussion indicates that the final atomic co-ordinates, derived by the minimisation procedure of the F_O — F_C synthesis, imply certain deviations from standard bond angles; some of these distortions are outside the limits of experimental error and are therefore real, while others can be removed by small shifts of atomic co-ordinates which lie within these limits.

The length of the central double bond of the ethylenic system is 1·31 Å. The lateral

bonds 10—12 and 10—14 are 1·54 and 1·52 Å long and enclose an angle of 113°. The doubly-bonded atom 10 does not lie in the plane defined by atoms 12 and 14 and the centre of symmetry but is displaced from it by 0·07 Å. This deviation from planarity is believed to lie within the experimental error, since a shift of atom 10 into this plane affects mainly its y co-ordinate.

The benzene rings A and B are rotated by 40° out of the plane of the ethylenic group. Both rings are planar, their atoms deviating by a maximum of 0·04 Å from their best planes.
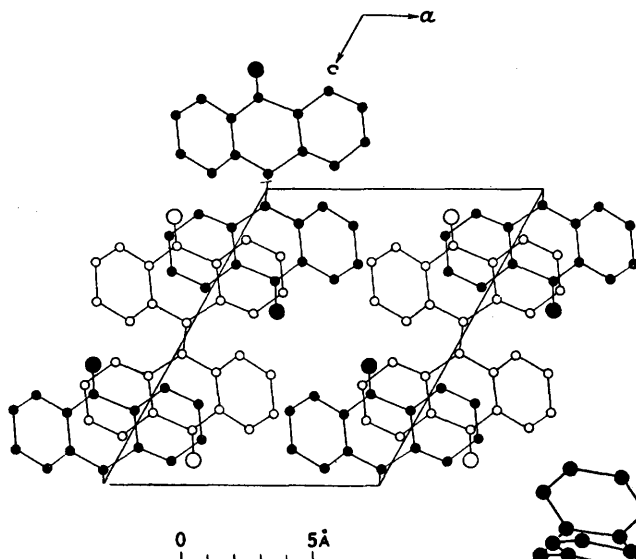
FIG. 4.   *The projection of the unit-cell contents on* (010).

FIG. 5.   *The projection of the unit-cell contents down* [100].
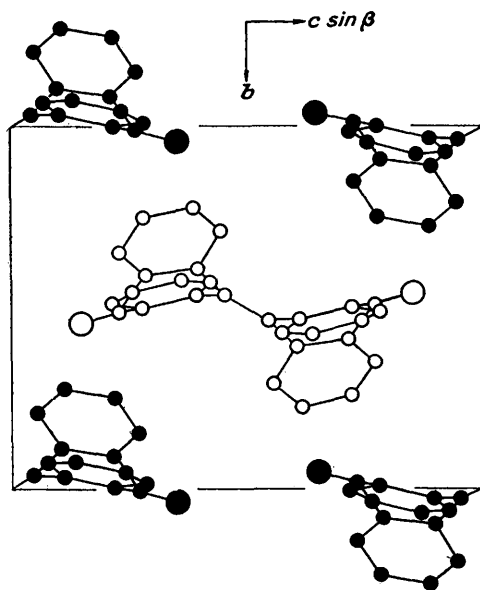
The bond lengths all lie within 0·06 Å of the mean value of 1·40 Å, and the bond angles within 3° of the mean value of 120°. The exocyclic bonds 10—12 and 10—14 to the central double bond both make angles of 2° with the planes of their respective benzene rings. This distortion is within the limit of experimental error; it depends chiefly upon the y co-ordinate of atom 10, in which a shift of 0·05 Å, in the same direction as that required to make the ethylenic system planar, would make both 2, 12, 10 and 6, 14, 10 collinear. The exocyclic bond 9—11 to the carbonyl group is inclined out of the plane of its benzene ring A so that it makes an angle of 7° with the prolongation of the ring diagonal 3—11, this angle lying in a plane perpendicular to the benzene ring. The corresponding angle between 9—13 and the plane of benzene ring B is 9°. These distortions are definitely beyond the limit of

experimental error since atom 9 would have to move by 0·18 Å in y in order to become collinear with 3—11 and 7—13. Furthermore, such a shift would stretch the exocyclic bonds 9—11 and 9—13 to 1·6 Å, make the oxygen atom lie 0·1 Å out of their plane, and compress the angle 11—9—13 to 106°.

The length of the double bond of the carbonyl group is 1·20 Å; the lateral bonds to the benzene rings are 1·52 and 1·51 Å long and enclose an angle of 116°. The four atoms of the carbonyl system are not strictly coplanar, as atom 9 is displaced by 0·07 Å and the oxygen atom by 0·06 Å from the most probable plane through 9, 11, 13 and the oxygen atom, but this apparent deviation from planarity is probably not significant as it involves primarily the y co-ordinates of the atoms.

The model of dianthronylidene deduced may be interpreted as consisting of a planar ethylenic group of central bond length 1·31 Å, attached to four phenyl groups by bonds which, owing to the angle of 40° between the planes of the ethylenic system and the benzene rings and the resulting absence of resonance interaction, have single-bond character (1·53 Å). The angle of twist is sufficient to produce a separation of 2·9 Å between carbon atoms 4 and 4′ and between carbon atoms 8 and 8′. With the lateral bonds of the ethylenic group making an angle of 113°, atoms 11 and 13 are 2·57 Å apart, permitting the insertion of the

FIG. 6. *A perspective view of the molecular model.*

FIG. 7. *The dimensions of the experimental model.*
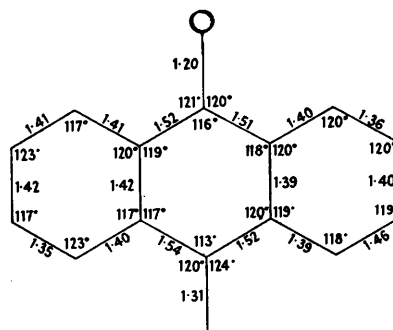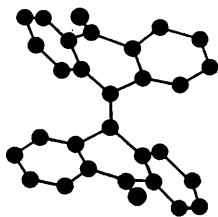
carbonyl bridge with C–C bond lengths of 1·52 Å and a C–C–C angle of 116°, but this involves distortion of the exocyclic bonds to the carbonyl carbon by about 8° out of the planes of their benzene rings. The structure of dianthronylidene thus resembles previously-analysed overcrowded structures in that the balance between intramolecular repulsion and forces due to bond distortion results in intramolecular approach distances of 2·9 Å, and that the distortions within the molecule are not localised but are distributed over several bonds.

The phenomena of thermochromy and photochromy (see, *e.g.*, Grubb and Kistiakowsky, *J. Amer. Chem. Soc.*, 1950, **72**, 419; Hirschberg and Fischer, *J.*, 1953, 629; Theilacker, Kortüm, and Friedheim, *Ber.*, 1950, **83**, 508) have been interpreted as evidence for the existence of more than one structure of dianthronylidene. In the absence of intermolecular carbon-to-carbon distances of less than 3·6 Å, it is unlikely that the structure determined here is to any appreciable extent affected by molecular packing in the crystal lattice. There is therefore no need to entertain the possibility of a change of configuration when the molecule passes from the crystalline to the dissolved state, and we assume that the ground state of dianthronylidene is correctly represented by the present model. We propose to discuss in a later paper possible structures for the excited state of dianthronylidene.

EXPERIMENTAL

Large crystals of dianthronylidene can be grown by slow cooling, over a week, of a solution in redistilled nitrobenzene. The crystals are monoclinic, yellow bipyramids elongated along [010], showing a variety of unidentified *hkl* faces. No previous data have been recorded; the entry in Groth's "Chemische Kristallographie," Leipzig, 1919, V, 440, under "Dianthron" refers to the dihydro-compound, dianthronyl.

The crystallographic constants were measured from zero-layer Weissenberg photographs about the three principal axes and corrected by extrapolation to $\theta = 90°$ (Buerger, " *X*-Ray Crystallography," John Wiley and Sons, 1942, Ch. 20). The space-group was identified as $P2_1/c$ from zero- and first-layer photographs about [010] and [100]. The zonal reflections were recorded on zero-layer Weissenberg photographs by the multiple-film technique, and their intensities estimated in the usual way. The $h0l$ intensities were estimated independently by two observers; agreement between the two sets of intensities was sufficiently good to indicate an accuracy of 10% in mean F($h0l$). The observed structure factors were placed on an approximately absolute scale by Wilson's method (*Nature*, 1942, **150**, 152); later comparison with calculated structure factors showed that the scale had been underestimated by about 20%. The crystals reflect *X*-rays well; in the $h0l$ zone out of the total number of reflections within the limiting sphere for Cu-$K\alpha$ radiation 81% were recorded.

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