

## The Structure of *trans*- $\alpha\beta$ -Dicyanostilbene

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*trans*- $\alpha\beta$ -Dicyanostilbene,  $C_6H_5 \cdot C(CN) : C(CN) \cdot C_6H_5$ , forms monoclinic crystals, space group  $C2/c$ , with a unit cell of dimensions

$$a = 17.98 \pm 0.05, b = 3.96 \pm 0.02, c = 17.23 \pm 0.05 \text{ \AA}, \beta = 91 \pm 0.5^\circ,$$

containing 4 molecules. The molecular structure, derived from Fourier projections along each of the three crystallographic axes, is non-planar. Approximate molecular dimensions are given and discussed in terms of conjugation.

### Derivation of the structure

The crystallographic investigation of  $\alpha\beta$ -dicyanostilbene  $C_6H_5 \cdot C(CN) : C(CN) \cdot C_6H_5$  was originally undertaken merely in order to determine whether the normal configuration of the molecule is *cis* or *trans*. The evidence which led to the conclusion that the molecule has the *trans* configuration has already been reported briefly (Timmons & Wallwork, 1955). It was based on refinement of the structure by means of Fourier projections. This report gives more detail of the crystallographic work and of the molecular structure found.

The crystal data are:

$$D_m = 1.242 \text{ g.cm.}^{-3}, D_x = 1.247 \text{ g.cm.}^{-3}.$$

Monoclinic, with

$$a = 17.98 \pm 0.05, b = 3.96 \pm 0.02, c = 17.23 \pm 0.05 \text{ \AA}, \\ \beta = 91 \pm 0.5^\circ; Z = 4.$$

Space group  $C2/c$  or  $Cc$ .  $F(000) = 480$ .

Zero-layer Weissenberg photographs were obtained with copper radiation for the crystal rotating about each of its axes. Intensities were determined visually, those for  $h0l$  being obtained from a crystal twinned across (001) since difficulty was experienced in finding crystals which were not twinned. Since an accurate structure determination was not contemplated, no attempt was made to obtain intensities of high accuracy. The statistical method of Howells, Phillips & Rogers (1950) applied to the  $h0l$  intensities was inconclusive but favoured the centrosymmetric structure. The space group was therefore assumed to be  $C2/c$ . If there had been no doubt about the centrosymmetric character of the structure the molecules would have been known to have the *trans* configuration because they would have had to occupy special positions requiring a molecular centre of symmetry. Although this could not be known with certainty at this stage it was assumed as a basis for obtaining a trial structure and the assumption was justified by the

refinement of the structure (particularly the  $h0l$  projection).

From the point of view of the  $h0l$  projection it is immaterial which set of four-fold centrosymmetric special positions is chosen. The molecules were therefore assumed to have their centres at  $000$ ,  $00\frac{1}{2}$ ,  $\frac{1}{2}\frac{1}{2}0$  and  $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ . The space group  $C2/c$  requires all the molecules to have the same orientation in this projection and this was deduced by consideration of the  $h0l$  weighted reciprocal lattice. This was assisted by the short  $b$  cell dimension which indicated that the benzene rings could not be far from perpendicular to the  $b$  axis. The atomic positions found in this way were refined mainly by Fourier syntheses and partly by a

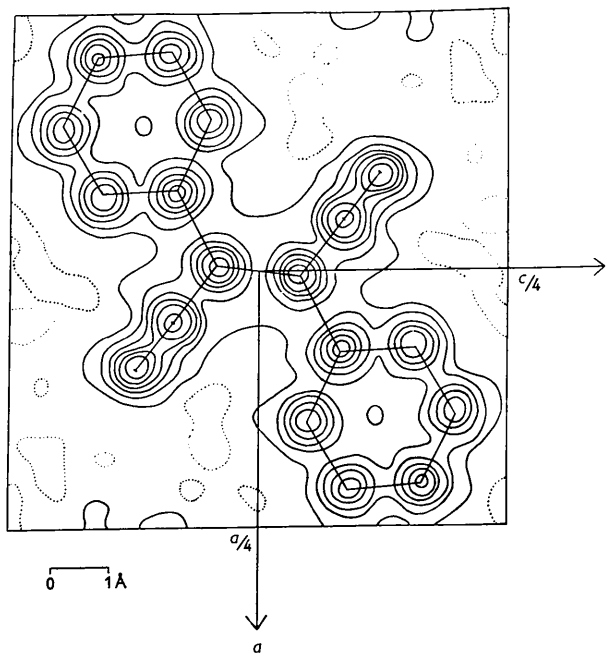


Fig. 1. Final Fourier  $h0l$  projection. Contours at intervals of  $1 \text{ e. \AA}^{-2}$ ; zero contour dotted.

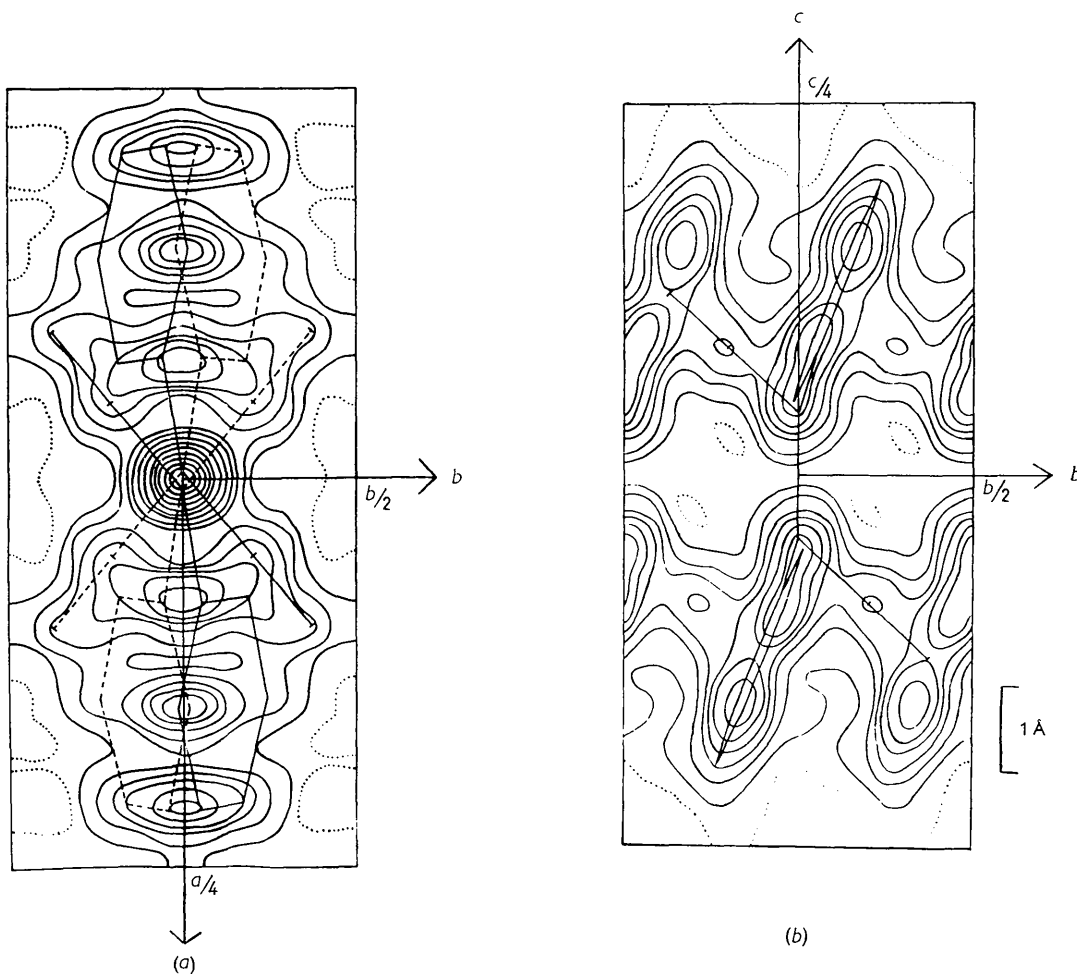


Fig. 2. Final Fourier  $hkl$  and  $Ok_l$  projections. Contours at intervals of  $2 \text{ e.}\text{\AA}^{-2}$ ; zero contour omitted,  $2 \text{ e.}\text{\AA}^{-2}$  contour dotted. Two overlapping molecules are indicated in the  $hkl$  projection.

few cycles of difference syntheses and gave finally the electron density map shown in Fig. 1.

In the later stages of the refinement, 7 intense reflections which consistently calculated too large were put into the Fourier syntheses as  $F_c$  rather than as  $F_o$  and the corresponding terms were omitted from the difference syntheses. No attempt was made to take the refinement beyond the stage of a common isotropic temperature factor  $B$  for all the atoms, and hydrogen atoms were not included in the calculations. In obtaining the residual  $R$ , one term ( $\bar{2}02$ ) was omitted because its high intensity could only be roughly estimated and a few strong reflections (marked with an asterisk in Table 2) were corrected for extinction by plotting  $I_c/I_o$  versus  $I_c$  and using the best straight line so obtained to read off  $I_o(\text{corr.})/I_o$  for each  $I_c$  (Pinnock, Taylor & Lipson, 1956). In this way, and with  $B=4.8 \text{ \AA}^2$ , the final value of  $R$  was 0.17.

By comparing projected interatomic distances with expected values it was found that the benzene rings

and the CN groups must all be tilted out of the planes parallel to (010). It was possible to deduce only approximate angles of tilt and it was not known whether each CN group was tilted in the same direction as the benzene ring adjacent to it, retaining a roughly planar molecule, or in the opposite direction. To investigate this point, refinement of the  $hkl$  and  $Ok_l$  projections was attempted by Fourier and difference methods though in each case there were only a few reflections because of the short  $b$  axis and there was

Table 1. Fractional atomic coordinates

Atom	$x$	$y$	$z$
C <sub>1</sub>	0.005	0	0.042
C <sub>2</sub>	-0.050	-0.200	0.085
C <sub>3</sub>	0.079	0.055	0.083
C <sub>4</sub>	0.075	0.184	0.158
C <sub>5</sub>	0.142	0.241	0.197
C <sub>6</sub>	0.208	0.170	0.164
C <sub>7</sub>	0.214	0.043	0.090
C <sub>8</sub>	0.148	-0.015	0.049
N	-0.095	-0.370	0.123

serious overlapping of atoms. In addition, it was necessary to consider an alternative set of special positions i.e.  $\frac{1}{4}\frac{1}{4}0$ ,  $\frac{3}{4}\frac{1}{4}\frac{1}{2}$ ,  $\frac{3}{4}\frac{3}{4}0$ ,  $\frac{1}{4}\frac{3}{4}\frac{1}{2}$ , and positions related to these by a change of origin, which only cause differences in magnitude for  $F_{hko}$ . It was found possible to exclude these alternatives at a fairly early stage in refinement of the  $hk0$  projection on the

grounds of much poorer agreement between  $F_o$  and  $F_c$ . The final Fourier  $hk0$  and  $0kl$  projections are shown in Fig. 2. As with the  $h0l$  projection,  $F_c$  was used in place of  $F_o$  for a few intense reflections and values of  $F_o$  corrected for extinction were used in the calculation of  $R$ . Final values of  $R$  (using  $B=3.8 \text{ \AA}^2$ ) were 0.19 and 0.16 for the  $hk0$  and  $0kl$  projections respectively.

Table 2. Observed and calculated structure factors

$hkl$	$F_o$	$F_c$	$hkl$	$F_o$	$F_c$	$hkl$	$F_o$	$F_c$	$hkl$	$F_o$	$F_c$
200	51*	51	$\bar{6}06$	18	-26	40,12	23	26	80,20	6	2
400	25	-33	406	9	-6	60,12	25	-22			
600	36	-33	$\bar{2}06$	49*	46	80,12	33	-34	110	94*	99
800	17	-19	006	21	-28	10,0,12	9	-7	310	13	-14
10,00	12	14	206	90*	-89	12,0,12	15	-11	510	44*	54
12,00	11	5	406	8	-11	14,0,12	<6	6	710	11	-10
14,00	49	42	606	52*	50	16,0,12	<5	1	910	8	8
16,00	15	-11	806	9	-9				11,10	8	-9
18,00	9	-5	10,06	<6	2	$\bar{1}6,0,14$	<5	5	13,10	30	27
20,00	11	8	12,06	<6	5	$\bar{1}4,0,14$	<5	3	15,10	25	22
22,00	<4	3	14,06	13	-7	$\bar{1}2,0,14$	<6	5	17,10	12	-6
			16,06	9	-4	$\bar{1}0,0,14$	22	-13	19,10	10	5
$\bar{2}2,02$	<4	-3				80,14	40	-43	21,10	6	-4
$\bar{2}0,02$	20	8	$\bar{1}6,08$	<6	-3	60,14	<7	3			
$\bar{1}8,02$	13	10	$\bar{1}4,08$	19	-23	40,14	<6	0	220	3	-1
$\bar{1}6,02$	26	30	$\bar{1}2,08$	9	4	20,14	<6	9	420	15	17
$\bar{1}4,02$	14	8	$\bar{1}0,08$	16	15	00,14	6	-4	620	17	16
$\bar{1}2,02$	8	-16	808	12	8	20,14	<6	8	820	13	17
$\bar{1}0,02$	10	8	608	<5	-11	40,14	16	-10	10,20	13	18
802	11	-15	408	15	17	60,14	29	-23	12,20	21	15
602	43*	47	208	24	21	80,14	22	23	14,20	19	9
402	22	-34	008	51*	-51	10,0,14	<6	2			
202	ca.160*	134	208	15	-16	12,0,14	9	-7	130	9	11
002	65*	66	408	26	-20	14,0,14	<5	-6	330	<4	-2
202	19	-27	608	33	-42	16,0,14	7	-3	530	<4	0
402	97*	102	808	18	-16	$\bar{1}4,0,16$	5	-5	730	13	18
602	9	-12	10,08	21	21	$\bar{1}2,0,16$	<5	3	930	9	13
802	19	28	12,08	<6	6	$\bar{1}0,0,16$	<6	-6	11,30	10	11
10,02	5	0	14,08	16	-15	80,16	<6	2	13,30	12	10
12,02	37	38	16,08	<6	-3	60,16	<6	-2			
14,02	<6	0				40,16	13	-10	020	7	10
16,02	28	-27	$\bar{1}6,0,10$	17	-12	20,16	<7	0	021	42*	-46
18,02	<6	2	$\bar{1}4,0,10$	20	-15	00,16	15	-11	022	62*	59
20,02	<5	-1	$\bar{1}2,0,10$	16	-13	20,16	<7	-1	023	17	-23
22,02	14	7	$\bar{1}0,0,10$	11	-4	40,16	19	-15	024	19	14
			80,10	27	31	60,16	13	9	025	32	32
$\bar{1}6,04$	21	15	60,10	15	-14	80,16	15	15	026	30	-35
$\bar{1}4,04$	14	14	40,10	12	-9	10,0,16	<6	1	027	7	2
$\bar{1}2,04$	<6	9	20,10	37	-41	12,0,16	<6	2	028	10	-5
$\bar{1}0,04$	23	-23	00,10	<5	-6	14,0,16	13	-7	029	13	-5
804	42	38	20,10	22	23				02,10	13	-12
604	65*	65	40,10	5	-7	80,18	<5	6	02,11	5	5
404	15	-8	60,10	10	-10	60,18	<6	2	02,12	9	-10
204	21	-20	80,10	36	-38	40,18	<6	0	02,13	8	-4
004	110*	-109	10,0,10	17	-14	20,18	18	-14	02,14	10	-8
204	11	12	12,0,10	13	-11	00,18	6	-4	02,15	5	-2
404	21	30	14,0,10	<6	2	20,18	<6	7	02,16	7	-2
604	97*	90	16,0,10	13	6	40,18	<6	0	02,17	4	2
804	49	48				60,18	<6	2			
10,04	20	-21	$\bar{1}6,0,12$	<5	0	80,18	<5	-2	040	16	12
12,04	<6	-3	$\bar{1}4,0,12$	<6	2				041	7	3
14,04	24	-20	$\bar{1}2,0,12$	13	-13	80,20	<4	4	042	11	7
16,04	<7	5	$\bar{1}0,0,12$	11	8	60,20	12	10	043	10	-11
			80,12	29	-29	40,20	<5	1	044	7	9
$\bar{1}6,06$	16	10	60,12	26	-28	20,20	<5	-1	045	10	-13
$\bar{1}4,06$	21	14	40,12	<6	7	00,20	<5	5	046	8	-5
$\bar{1}2,06$	<6	0	20,12	13	-13	20,20	<5	-1	047	15	14
$\bar{1}0,06$	18	16	00,12	16	9	40,20	<5	-2	048	11	-13
806	30	27	20,12	<6	-3	60,20	<4	3	049	13	13

\* denotes  $F_o$  corrected for extinction

Values of  $F_o$  and  $F_c$  for all three projections are given in Table 2.

### Results and discussion

Table I shows the final atomic coordinates. In view of the poor resolution of the  $hk0$  and  $0kl$  projections the  $y$  coordinates are only regarded as being very approximate. The  $x$  and  $z$  coordinates are more accurate and mean values of the standard deviations calculated by Cruickshank's (1949) method give  $\sigma_{x,z}$  as 0.015 Å for C and 0.023 Å for N, though these values may be an under-estimate in view of the quality of the intensity data. Because of the inaccuracy of the  $y$  coordinates both the actual (approximate) bond lengths and angles and the more accurate projected values of the bond lengths from the  $h0l$  syntheses are shown together in Fig. 3.

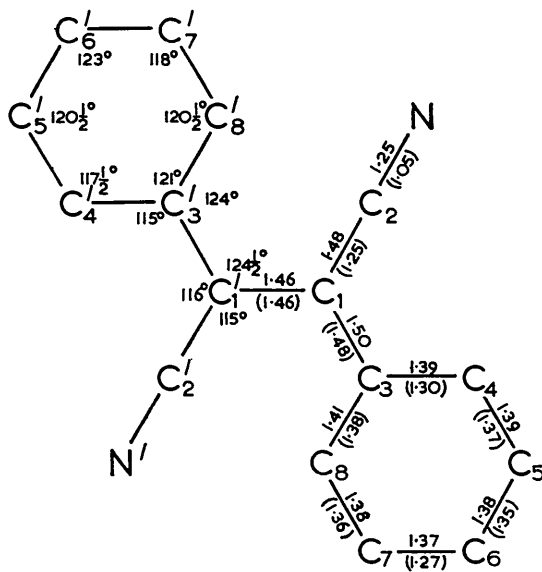


Fig. 3. Molecular dimensions. Values in parentheses are interatomic distances seen in projection on (010).

The molecule, although confirmed as having the *trans* configuration, is definitely non-planar. The linear C<sub>1</sub>-C<sub>2</sub>-N group is tilted about 24° out of the plane formed by the atoms C<sub>3</sub>C<sub>1</sub>C<sub>3</sub>. This is presumably caused by the necessity of avoiding close contacts with the adjacent benzene ring. This view is supported by the fact that the ring is twisted about its C<sub>3</sub>C<sub>6</sub> axis through about 25° so as to increase further the distance between C<sub>2</sub> and C<sub>4</sub> which is still only about 2.96 Å. The only other close approach within the molecule is C<sub>8</sub> to C<sub>2</sub> which is about 3.01 Å. Intermolecular contacts are all normal. The molecule as a whole appears to be twisted about its central C-C bond such that the C<sub>1</sub>C<sub>3</sub>C<sub>6</sub> direction is inclined at about 8° to the (010) plane.

The individual C-C distances in the benzene ring do not differ significantly from the mean value of 1.39 Å. There is evidence of conjugation of the central C-C bond of the molecule both with the benzene rings and with the CN groups. This is found even if only the projected bond lengths are considered by comparing the ratio of C<sub>1</sub>-C<sub>3</sub> to the length of the bonds parallel to it in the benzene ring with the ratio 1.52:1.39 expected if there were no conjugation, and by comparing similarly the ratio C<sub>1</sub>-C<sub>2</sub>:C<sub>2</sub>-N with the expected 1.50:1.16. (For this discussion, single bond radii for carbon in various states of hybridization have been calculated from the data of Wilms-hurst (1960).) If the actual bond lengths are accepted as being approximately correct both C<sub>1</sub>-C<sub>3</sub> and C<sub>1</sub>-C<sub>2</sub> are found to be shorter than  $sp^2-sp^2$  and  $sp^2-sp$  single bonds respectively, C<sub>2</sub>-N is longer than a triple C-N bond and C<sub>1</sub>-C<sub>1</sub>' is longer than a double C-C bond. Indeed, the central bond would appear to have only a small amount of double-bond character and it may be that the development of positive charge on both C<sub>1</sub> and C<sub>1</sub>' by conjugation with the CN groups is tending to increase this length. Infra-red and ultra-violet spectroscopic studies of this compound by Felton & Orr (1955), Coe, Gale, Linstead & Timmons (1957), Williams & Le Fèvre (1957), and Timmons (1960) are in general agreement with these conclusions. The position (2225 cm.<sup>-1</sup>) of the C≡N stretching frequency indicates some conjugation with the rest of the molecule and the ultra-violet spectra indicate extensive conjugation involving the whole molecule. The decrease in intensity of the long-wavelength (*K*) band compared with that for *trans*-stilbene is consistent with the observed non-planarity of the molecule.

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### References

- COE, D. G., GALE, M. M., LINSTAD, R. P. & TIMMONS, C. J. (1957). *J. Chem. Soc.* p. 123.  
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.  
 FELTON, D. G. I. & ORR, S. F. D. (1955). *J. Chem. Soc.* p. 2170.  
 HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.  
 PINNOCK, P. R., TAYLOR, C. A. & LIPSON, H. (1956). *Acta Cryst.* **9**, 173.  
 TIMMONS, C. J. (1960). Private communication.  
 TIMMONS, C. J. & WALLWORK, S. C. (1955). *Chem. and Ind.* p. 62.  
 WILLIAMS, A. J. & LE FÈVRE, R. J. W. (1957). *J. Chem. Soc.* p. 2425.  
 WILMSHURST, J. K. (1960). *J. Chem. Phys.* **33**, 813.