

## References

- BOX, H. C., FREUND, H. G., LILGA, K. T. & BUDZINSKI, E. E. (1970). *J. Phys. Chem.* **74**, 40–52.
- FURNAS, T. C. JR & HARKER, D. (1955). *Rev. Sci. Instrum.* **26**, 449–453.
- International Tables for X-ray Crystallography* (1967). Vol. II, 2nd ed., pp. 300–306. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1968). Vol. III, 2nd ed., pp. 166, 202–207, 214. Birmingham: Kynoch Press.
- IUPAC-IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *J. Mol. Biol.* **52**, 1–17.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
- PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 260. Ithaca: Cornell Univ. Press.
- PETERSON, J., STEINRAUF, L. K. & JENSEN, L. H. (1960). *Acta Cryst.* **13**, 104–109.
- ROSENFELD, R. E. JR (1974). *Investigation of the Crystal Structures of Amino Acids Containing Sulfur*. Dissertation, State Univ. of New York at Buffalo.
- ROSENFELD, R. E. JR & PARTHASARATHY, R. (1974). *J. Amer. Chem. Soc.* **96**, 1925–1930.
- ROSENFELD, R. E. JR & PARTHASARATHY, R. (1975). *Acta Cryst.* **B31**, 462–468.
- STEINRAUF, L. K., PETERSON, J. & JENSEN, L. H. (1958). *J. Amer. Chem. Soc.* **80**, 3835–3838.

*Acta Cryst.* (1975). **B31**, 819

## Optical Induction in Chiral Crystals. II.\* The Crystal and Molecular Structures of 1-(2,6-Dichlorophenyl)-4-phenyl-*trans,trans*-1,3-butadiene

BY D. RABINOVICH AND Z. SHAKKED

*Department of Structural Chemistry, Weizmann Institute of Science, Rehovot, Israel*

(Received 21 August 1974; accepted 24 October 1974)

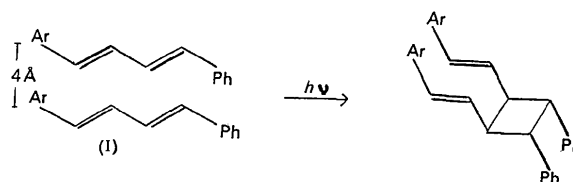
The title compound ( $C_{16}H_{12}Cl_2$ ) crystallizes in space group  $P2_12_12_1$  with  $a=9.3881$  (2),  $b=4.0286$  (1) and  $c=35.3073$  (3) Å,  $Z=4$ . The structure has been determined by direct methods from three-dimensional diffractometer data collected with Cu  $K\alpha$  radiation, and refined to  $R=0.04$ . The absolute configuration of the molecules in the analysed crystal was determined by the anomalous scattering of the chlorine atoms. The rotations of the phenyl and the dichlorophenyl groups from the butadiene plane are  $15^\circ$  and  $40^\circ$  respectively. The molecular conformation is believed to control the exclusive photoreactivity of the double bond adjacent to the phenyl ring and the formation of an optically active heterodimer in a mixed single crystal of the title compound with its thiophene analogue.

### Introduction

Two of the necessary conditions for optical synthesis discussed in part I (Rabinovich & Shakked, 1974), chiral space group and *prochiral* conformation, were observed in the designing of another asymmetric synthesis experiment, namely, the photodimerization of parallel C=C double bonds stacked along a short (*ca* 4 Å) axis. Irradiation of such a system yields a cyclobutane possessing a mirror plane (Schmidt, 1967). However, as was suggested by Lahav (1968), the irradiation of a chiral single crystal containing a guest molecular species may lead to the formation of unequal amounts of enantiomeric heterodimers if the molecules are heavily distorted from planarity.

The present analysis deals with the crystal and molecular structures of 1-(2,6-dichlorophenyl)-4-phenyl-*trans,trans*-1,3-butadiene (I) which crystallizes in a chiral space group ( $P2_12_12_1$ ) with a short (4.03 Å) axis and is expected to possess a pronounced *prochiral* con-

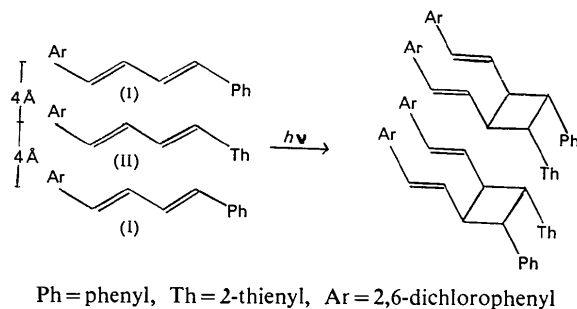
formation due to the two *ortho*-substituted chlorines. This compound yields under irradiation a single cyclobutane resulting from exclusive dimerization at the double bond adjacent to the phenyl ring (Cohen, Elgavi, Green, Ludmer & Schmidt, 1972).



Ph = phenyl, Ar = 2,6-dichlorophenyl

(I) and its thiophene analogue [1-(2,6-dichlorophenyl)-4-thienyl-*trans,trans*-1,3-butadiene, (II)] are isomorphous and show extensive solid solubility. Irradiation of a mixed single crystal of (I) and (II) (approximate ratio 4:1) in the thienyl absorbing wavelength range yields one of the two enantiomeric heterodimers in excess (Elgavi, 1973; Elgavi, Green & Schmidt, 1973).

\* Part I: Rabinovich & Shakked (1974).



The structure analysis of (I) was needed in order to explain both the exclusive photoreactivity of one of the two available double bonds and the formation of an optically active product in the mixed crystal system.

### Experimental

Crystals of (I) (Fig. 1) were grown by slow evaporation of ethyl acetate solutions. The colourless crystals are elongated along [010]. A nearly equidimensional crystal was obtained by cleaving a needle-shaped crystal.

The crystal was mounted along [010] on a General Electric diffractometer. Accurate cell dimensions were derived by a least-squares procedure using high-order reflexions measured with Cu  $K\alpha$  radiation ( $2\theta > 120^\circ$ ). Crystal data are listed in Table 1.

Table 1. *Crystal data*

1-(2,6-Dichlorophenyl)-4-phenyl- <i>trans,trans</i> -1,3-butadiene,	
C <sub>16</sub> H <sub>12</sub> Cl <sub>2</sub> , m.p. 108°	
Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> M.W. 275.1	
<i>a</i> = 9.3881 (2) Å	<i>D</i> <sub>x</sub> = 1.37 g cm <sup>-3</sup> for <i>Z</i> = 4
<i>b</i> = 4.0286 (2)	<i>D</i> <sub>m</sub> = 1.36 g cm <sup>-3</sup>
<i>c</i> = 35.3073 (3)	$\mu(\text{Cu } K\alpha) = 41.6 \text{ cm}^{-1}$

Three-dimensional intensity data ( $2\theta \leq 160^\circ$ , one octant of the reciprocal sphere, 1787 reflexions) were

Table 2. *Fractional coordinates and vibration tensor components (Å<sup>2</sup>) of the heavy atoms and their e.s.d.'s*

The anisotropic temperature factor is of the form:  $\exp[-2\pi^2(h_i a^i)(h_j a^j) U^{ij} \times 10^{-4}]$ , where  $h_i$  and  $a^i$ ,  $i = 1, 2, 3$  are reflexion indices and reciprocal unit-cell edges respectively.

	<i>x</i> (× 10 <sup>4</sup> )	<i>y</i> (× 10 <sup>4</sup> )	<i>z</i> (× 10 <sup>5</sup> )	<i>U</i> <sup>11</sup>	<i>U</i> <sup>22</sup>	<i>U</i> <sup>33</sup>	<i>U</i> <sup>12</sup>	<i>U</i> <sup>23</sup>	<i>U</i> <sup>13</sup>
C(1)	2218 (4)	3647 (11)	-8966 (8)	726 (23)	711 (27)	394 (15)	-76 (25)	-39 (19)	12 (16)
C(2)	1017 (4)	5311 (10)	-7750 (8)	604 (20)	698 (27)	462 (16)	-25 (22)	86 (19)	-81 (15)
C(3)	849 (3)	6077 (9)	-3965 (8)	524 (18)	565 (24)	483 (16)	29 (20)	31 (17)	-29 (14)
C(4)	1865 (3)	5142 (9)	-1297 (7)	473 (16)	466 (20)	368 (13)	-53 (16)	26 (15)	-10 (12)
C(5)	3053 (3)	3402 (10)	-2570 (8)	462 (16)	577 (23)	466 (15)	13 (19)	3 (17)	-53 (13)
C(6)	3233 (4)	2683 (11)	-6360 (9)	557 (20)	730 (29)	507 (17)	5 (21)	-116 (20)	55 (15)
C(7)	1634 (3)	6113 (10)	2665 (8)	512 (17)	519 (23)	437 (15)	-8 (19)	-32 (16)	38 (13)
C(8)	2332 (3)	4971 (9)	5717 (8)	554 (18)	495 (19)	378 (14)	-82 (19)	-12 (15)	22 (13)
C(9)	2015 (3)	6212 (9)	9490 (8)	586 (18)	493 (22)	405 (14)	-50 (19)	-9 (16)	13 (14)
C(10)	2653 (3)	5135 (10)	12624 (8)	608 (20)	514 (21)	400 (15)	-38 (20)	-14 (16)	40 (14)
C(11)	2441 (3)	6465 (9)	16468 (7)	609 (17)	433 (18)	364 (13)	-48 (18)	29 (14)	-20 (12)
C(12)	1123 (3)	7413 (9)	17988 (8)	611 (19)	558 (23)	408 (15)	-52 (19)	-1 (16)	-24 (14)
C(13)	981 (4)	8755 (11)	21582 (9)	682 (21)	658 (26)	492 (17)	-9 (24)	-19 (20)	51 (17)
C(14)	2168 (4)	9140 (11)	23829 (9)	888 (26)	752 (31)	436 (17)	-10 (26)	-11 (20)	17 (18)
C(15)	3483 (4)	8141 (12)	22533 (9)	830 (26)	791 (29)	407 (17)	-54 (27)	-30 (20)	-10 (17)
C(16)	3592 (3)	6848 (10)	18928 (8)	615 (20)	571 (23)	445 (15)	29 (20)	60 (18)	-26 (14)
Cl(26)	-444 (1)	6817 (3)	15496 (2)	590 (5)	1183 (9)	623 (5)	-79 (7)	-147 (6)	-8 (4)
Cl(30)	5290 (1)	5703 (3)	17434 (2)	642 (5)	1193 (10)	531 (4)	148 (7)	29 (6)	-55 (4)

collected manually by the stationary-counter stationary-crystal technique. The measurements were made at room temperature with Ni-filtered Cu  $K\alpha$  radiation. The intensities of four standard reflexions were monitored every 100 reflexions throughout the data collection. The overall reduction in the intensity due to crystal deterioration was about 6%. The intensities were corrected for Lorentz, polarization and absorption effects. The weighting factors  $w(hkl)$  and assignment of unobserved reflexions were derived by a procedure previously described (Filippakis, Leisero-witz & Schmidt, 1967).

### Structure solution and refinement

The structure was solved by a multi-solution technique utilizing the tangent formula (Kaufman & Leisero-witz, 1970). An *E* map based on the phases of the model with the lowest (0.29)  $R_{\text{Karle}}$  (Karle & Karle, 1966) yielded all the non-hydrogen atoms in the molecule. These atoms were refined isotropically by a full-matrix least-squares program. Eventually, all hydrogens were inserted in chemically reasonable positions and the structure was further refined (anisotropically

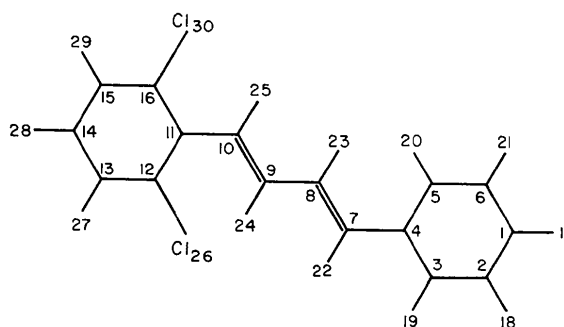


Fig. 1. 1-(2,6-Dichlorophenyl)-4-phenyl-*trans,trans*-1,3-butadiene (I). Chemical formula and numbering of atoms.

for carbon and chlorine, and isotropically for the hydrogen atoms) by a block-diagonal least-squares program to the following agreement values:

$$R = \frac{\sum kF_o - |F_c|}{\sum kF_o} = 0.040$$

$$r = \frac{\sum w(k^2F_o^2 - |F_c|^2)}{\sum wk^4F_o^4} = 0.006.$$

The number of refined parameters and the number of observations included in the last cycle of refinement were 211 and 1520 respectively.

The scattering factors used are those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for C, Dawson (1960) for Cl and McWeeny (1951) for H. Next, anomalous dispersion corrections were introduced for Cl, the values used ( $\Delta f' = 0.3$ ,  $\Delta f'' = 0.7$ ) being taken from *International Tables for X-ray Crystallography* (1962). Refinements of both enantiomorphic structures were carried on until the shifts of the parameters were less than  $0.2\sigma$ . Final agreement values of the two enantiomorphs are as follows:

$$R = 0.037, 0.047$$

$$r = 0.004, 0.008.$$

The coordinates and thermal parameters of the two enantiomorphic structures agree within  $2\sigma$ .

Use of the *R* test (Hamilton, 1965) indicates that the difference is highly significant and the choice of handedness implied by the parameters in Table 2 with a right-handed coordinate system is correct. In this context however (of flexible molecules undergoing spontaneous resolution) the chirality indicated by these results is merely a consequence of the arbitrary choice of a crystal; it has no chemical significance. The final parameters and their e.s.d.'s are listed in Tables 2 and 3. A list of observed and calculated structure factors is given in Table 4.

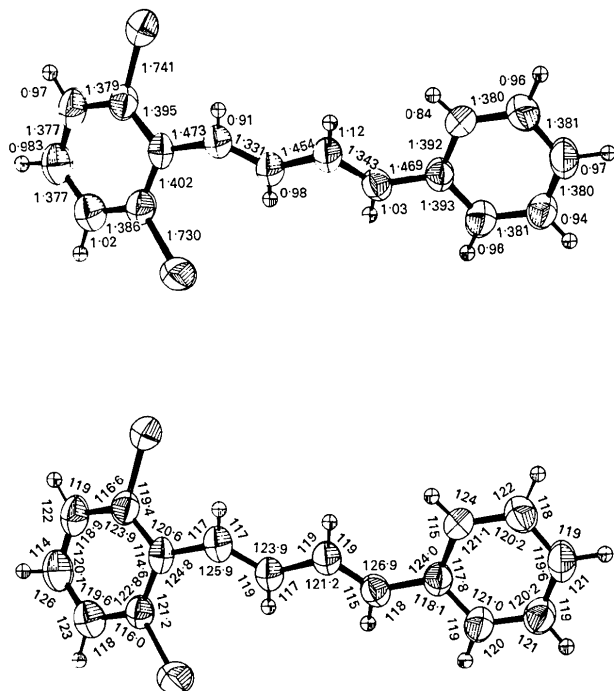


Fig. 2. Bond lengths (Å) and angles (°). The thermal ellipsoids are drawn at 50% probability level (Johnson, 1965). The view is along the *b* axis.

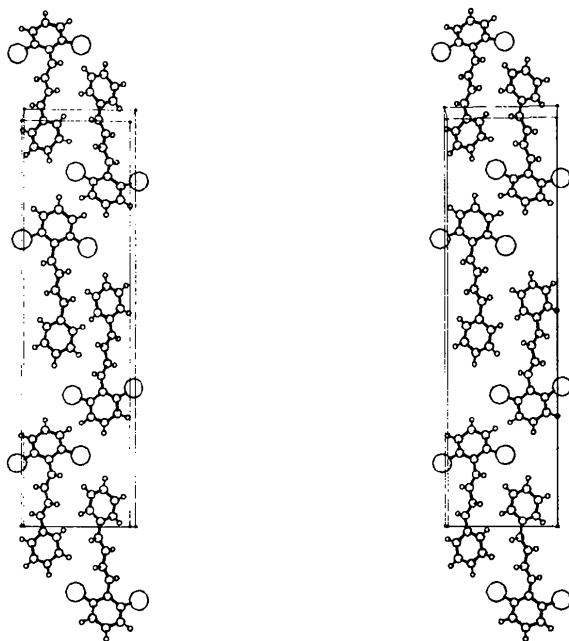


Fig. 3. Stereoscopic view of the packing arrangement along the *b* axis. The origin of the unit cell is in the bottom left-hand corner with *c* axis vertical and *a* axis horizontal and *b* entering the paper.

Table 3. *Hydrogen atom parameters and their e.s.d.'s*

	$x(\times 10^3)$	$y(\times 10^3)$	$z(\times 10^4)$	$\bar{U}^2(\times 10^3 \text{ \AA}^2)$
H(17)	236 (3)	313 (9)	-1162 (8)	33 (9)
H(18)	33 (3)	598 (9)	-953 (8)	33 (10)
H(19)	3 (3)	726 (9)	-312 (8)	35 (11)
H(20)	365 (3)	295 (10)	-88 (7)	25 (10)
H(21)	408 (3)	161 (11)	-729 (9)	56 (12)
H(22)	92 (3)	780 (10)	319 (8)	34 (10)
H(23)	304 (3)	273 (8)	539 (7)	12 (8)
H(24)	130 (3)	797 (11)	970 (8)	39 (11)
H(25)	335 (3)	358 (9)	1232 (7)	24 (9)
H(27)	-1 (3)	942 (9)	2245 (7)	31 (10)
H(28)	218 (4)	1001 (11)	2643 (10)	67 (13)
H(29)	434 (3)	842 (9)	2404 (8)	37 (10)

## Results and discussion

### *Thermal motion analysis*

Least-squares analysis of the possible rigid-body motion of the molecule was carried out by the method of Schomaker & Trueblood (1968). Three rigid-body models were used, comprising different groups of atoms: the first model consisting of all non-hydrogen atoms, the second, of the atoms of the dichlorophenyl group and the central butadiene chain, and the third of the phenyl ring and the butadiene chain. The r.m.s.

values of  $\Delta U^{ij}$  (corrected for the number of degrees of freedom) obtained for the three models are: 0.0053, 0.0049 and 0.0039  $\text{\AA}^2$  respectively, significantly higher than the mean value (0.0018  $\text{\AA}^2$ ) of  $\sigma(U^{ij})$ . These figures show that none of the models properly represents rigid-body motion. The best fit is obtained for the third model, indicating that the internal vibrations centre mainly at the single bond adjacent to the dichlorophenyl group. The results of the analysis of the

first model are given in Table 5. The translational vibrations are nearly isotropic; the librational motion is highly anisotropic with the largest libration ( $5.5^\circ$ ) about the longest molecular axis. The results of the analysis of the second model are similar. The third model, however, yields a smaller librational motion ( $4.7^\circ$ ) about the longest axis of the molecule, thus substantiating our former indication about the internal vibrations of the molecule.

Table 4. Observed and calculated structure factors

Each set of three columns contains respectively  $I$ ,  $10F_o$  and  $10F_c$ . Unobserved reflexions are marked by  $U$  and zero-weighted reflexions by an asterisk.

$h$	$k$	$l$	$I$	$10F_o$	$10F_c$
1	2	1	127	127	127
1	2	2	144	144	144
1	2	3	159	159	159
1	2	4	174	174	174
1	2	5	189	189	189
1	2	6	204	204	204
1	2	7	219	219	219
1	2	8	234	234	234
1	2	9	249	249	249
1	2	10	264	264	264
1	2	11	279	279	279
1	2	12	294	294	294
1	2	13	309	309	309
1	2	14	324	324	324
1	2	15	339	339	339
1	2	16	354	354	354
1	2	17	369	369	369
1	2	18	384	384	384
1	2	19	399	399	399
1	2	20	414	414	414
1	2	21	429	429	429
1	2	22	444	444	444
1	2	23	459	459	459
1	2	24	474	474	474
1	2	25	489	489	489
1	2	26	504	504	504
1	2	27	519	519	519
1	2	28	534	534	534
1	2	29	549	549	549
1	2	30	564	564	564
1	2	31	579	579	579
1	2	32	594	594	594
1	2	33	609	609	609
1	2	34	624	624	624
1	2	35	639	639	639
1	2	36	654	654	654
1	2	37	669	669	669
1	2	38	684	684	684
1	2	39	699	699	699
1	2	40	714	714	714
1	2	41	729	729	729
1	2	42	744	744	744
1	2	43	759	759	759
1	2	44	774	774	774
1	2	45	789	789	789
1	2	46	804	804	804
1	2	47	819	819	819
1	2	48	834	834	834
1	2	49	849	849	849
1	2	50	864	864	864
1	2	51	879	879	879
1	2	52	894	894	894
1	2	53	909	909	909
1	2	54	924	924	924
1	2	55	939	939	939
1	2	56	954	954	954
1	2	57	969	969	969
1	2	58	984	984	984
1	2	59	999	999	999
1	2	60	1014	1014	1014
1	2	61	1029	1029	1029
1	2	62	1044	1044	1044
1	2	63	1059	1059	1059
1	2	64	1074	1074	1074
1	2	65	1089	1089	1089
1	2	66	1104	1104	1104
1	2	67	1119	1119	1119
1	2	68	1134	1134	1134
1	2	69	1149	1149	1149
1	2	70	1164	1164	1164
1	2	71	1179	1179	1179
1	2	72	1194	1194	1194
1	2	73	1209	1209	1209
1	2	74	1224	1224	1224
1	2	75	1239	1239	1239
1	2	76	1254	1254	1254
1	2	77	1269	1269	1269
1	2	78	1284	1284	1284
1	2	79	1299	1299	1299
1	2	80	1314	1314	1314
1	2	81	1329	1329	1329
1	2	82	1344	1344	1344
1	2	83	1359	1359	1359
1	2	84	1374	1374	1374
1	2	85	1389	1389	1389
1	2	86	1404	1404	1404
1	2	87	1419	1419	1419
1	2	88	1434	1434	1434
1	2	89	1449	1449	1449
1	2	90	1464	1464	1464
1	2	91	1479	1479	1479
1	2	92	1494	1494	1494
1	2	93	1509	1509	1509
1	2	94	1524	1524	1524
1	2	95	1539	1539	1539
1	2	96	1554	1554	1554
1	2	97	1569	1569	1569
1	2	98	1584	1584	1584
1	2	99	1599	1599	1599
1	2	100	1614	1614	1614
1	2	101	1629	1629	1629
1	2	102	1644	1644	1644
1	2	103	1659	1659	1659
1	2	104	1674	1674	1674
1	2	105	1689	1689	1689
1	2	106	1704	1704	1704
1	2	107	1719	1719	1719
1	2	108	1734	1734	1734
1	2	109	1749	1749	1749
1	2	110	1764	1764	1764
1	2	111	1779	1779	1779
1	2	112	1794	1794	1794
1	2	113	1809	1809	1809
1	2	114	1824	1824	1824
1	2	115	1839	1839	1839
1	2	116	1854	1854	1854
1	2	117	1869	1869	1869
1	2	118	1884	1884	1884
1	2	119	1899	1899	1899
1	2	120	1914	1914	1914
1	2	121	1929	1929	1929
1	2	122	1944	1944	1944
1	2	123	1959	1959	1959
1	2	124	1974	1974	1974
1	2	125	1989	1989	1989
1	2	126	2004	2004	2004
1	2	127	2019	2019	2019
1	2	128	2034	2034	2034
1	2	129	2049	2049	2049
1	2	130	2064	2064	2064
1	2	131	2079	2079	2079
1	2	132	2094	2094	2094
1	2	133	2109	2109	2109
1	2	134	2124	2124	2124
1	2	135	2139	2139	2139
1	2	136	2154	2154	2154
1	2	137	2169	2169	2169
1	2	138	2184	2184	2184
1	2	139	2199	2199	2199
1	2	140	2214	2214	2214
1	2	141	2229	2229	2229
1	2	142	2244	2244	2244
1	2	143	2259	2259	2259
1	2	144	2274	2274	2274
1	2	145	2289	2289	2289
1	2	146	2304	2304	2304
1	2	147	2319	2319	2319
1	2	148	2334	2334	2334
1	2	149	2349	2349	2349
1	2	150	2364	2364	2364
1	2	151	2379	2379	2379
1	2	152	2394	2394	2394
1	2	153	2409	2409	2409
1	2	154	2424	2424	2424
1	2	155	2439	2439	2439
1	2	156	2454	2454	2454
1	2	157	2469	2469	2469
1	2	158	2484	2484	2484
1	2	159	2499	2499	2499
1	2	160	2514	2514	2514
1	2	161	2529	2529	2529
1	2	162	2544	2544	2544
1	2	163	2559	2559	2559
1	2	164	2574	2574	2574
1	2	165	2589	2589	2589
1	2	166	2604	2604	2604
1	2	167	2619	2619	2619
1	2	168	2634	2634	2634
1	2	169	2649	2649	2649
1	2	170	2664	2664	2664
1	2	171	2679	2679	2679
1	2	172	2694	2694	2694
1	2	173	2709	2709	2709
1	2	174	2724	2724	2724
1	2	175	2739	2739	2739
1	2	176	2754	2754	2754
1	2	177	2769	2769	2769
1	2	178	2784	2784	2784
1	2	179	2799	2799	2799
1	2	180	2814	2814	2814
1	2	181	2829	2829	2829
1	2	182	2844	2844	2844
1	2	183	2859	2859	2859
1	2	184	2874	2874	2874
1	2	185	2889	2889	2889
1	2	186	2904	2904	2904
1	2	187	2919	2919	2919
1	2	188	2934	2934	2934
1	2	189	2949	2949	2949
1	2	190	2964	2964	2964
1	2	191	2979	2979	2979
1	2	192	2994	2994	2994
1	2	193	3009	3009	3009
1	2	194	3024	3024	3024
1	2	195	3039	3039	3039
1	2	196	3054	3054	3054
1	2	197	3069	3069	3069
1	2	198	3084	3084	3084
1	2	199	3099	3099	3099
1	2	200	3114	3114	3114
1	2	201	3129	3129	3129
1	2	202	3144	3144	3144
1	2	203	3159	3159	3159
1	2	204	3174	3174	3174
1	2	205	3189	3189	3189
1	2	206	3204	3204	3204
1	2	207	3219	3219	3219
1	2	208	3234	3234	3234
1	2	209	3249	3249	3249
1	2	210	3264	3264	3264
1	2	211	3279	3279	3279
1	2	212	3294	3294	3294
1	2	213	3309	3309	3309
1	2	214	3324	3324	3324
1	2	215	3339	3339	3339
1	2	216	3354	3354	3354
1	2	217	3369	3369	3369
1	2	218	3384	3384	3384
1	2	219	3399	3399	3399
1	2	220	3414	3414	3414
1	2	221	3429	3429	3429
1	2	222	3444	3444	3444
1	2	223	3459	3459	3459
1	2	224	3474	3474	3474
1	2	225	3489	3489	3489
1	2	226	3504	3504	3504
1	2	227	3519	3519	3519
1	2	228	3534	3534	3534
1	2	229	3549	3549	3549
1	2	230	3564	3564	3564
1	2	231	3579	35	

Table 5. Results of rigid-body motion analysis

The eigenvectors of **L** and **T** are referred to the molecular system of inertia **I** (in terms of the corresponding direction cosines  $\times 10^4$ ). The eigenvectors of **I** are referred to the reciprocal vectors  $a^*$ ,  $b^*$  and  $c^*$ . Components of the origin shifts  $q(\varrho_1, \varrho_2, \varrho_3)$ , referred to the molecular centroids are given in Å.

Eigenvalues		Eigenvectors		
663 (at. wt. Å <sup>2</sup> )		0.601	0.533	34.923
3721		<b>I</b> 9.251	-0.666	-1.470
4337		1.483	3.937	-4.978
(5.5°)*	92 ( $\times 10^{-4}$ rad <sup>2</sup> )	9997	-97	211
(1.6)	8	<b>L</b> 96	-6536	-7568
(1.4)	6	212	7568	-6534
(0.22 Å)	502 ( $\times 10^{-4}$ Å <sup>2</sup> )	-1827	9314	-3150
(0.21)	436	<b>T</b> -893	-2911	-3429
(0.20)	403	-411	2186	8850

$$q(-1.44, 0.01, 0.12) \\ [(\sum(\Delta U^i)^2)/(6n-s)]^{1/2} = 0.0053 \text{ Å}^2 \quad (n=18, s=20)$$

\* The corresponding r.m.s. amplitudes are given in parentheses.

### Molecular geometry

Fig. 2 shows the experimental bond lengths and angles, uncorrected for librational motion. The mean values of the e.s.d.'s in the bond lengths of C-Cl, C-C and C-H are 0.003, 0.004 and 0.03 Å respectively. The corresponding values for bond angles are 0.2, 0.3 and 1.8°. The 'bond-scatter'  $\{[\sum(r_i - \bar{r})^2/(n-1)]^{1/2}, \bar{r} = 1.385 \text{ Å}\}$  of the 12 aromatic bonds (0.008 Å) is significantly larger than the average e.s.d. (0.004 Å), probably due to the relative elongation of the four aromatic bonds adjacent to the butadiene chain. The 'bond scatter' value obtained without these bonds is 0.003 Å. The C-Cl bond lengths (1.741, 1.730 Å) agree well with the mean value (1.737  $\pm$  0.016 Å) given by Palenik, Donohue & Trueblood (1968).

The 'angle scatter' (defined analogously to the 'bond scatter') calculated from the 12 aromatic bond angles (2.3°) is much larger than the average e.s.d. (0.3°), indicating significant deviations from 120°. The largest deviations are observed at C(12), C(16) and C(11). The

first two values (122.8, 123.9°) are attributed to the chlorine substituents, since an aromatic substitution by electron-withdrawing groups generally leads to an increase in the internal angle at the substituted position. This effect has been observed in chlorine substitution as well (Hope, 1969; Bernstein, 1972). The remarkably small value (114.6°) of the aromatic angle at C(11) results from the substitution effect of the conjugated chain similarly to that observed at C(4) of the phenyl ring (117.8°), and from the narrowing which takes place to compensate for the widening at C(12) and C(16). Similar decreased values are observed in other *meta*-disubstituted benzene derivatives by electron-withdrawing groups (Trotter & Williston, 1966; Palenik *et al.*, 1968; Hope, 1969; Bavoux & Thozet, 1973).

The central C-C bond (1.454 Å) of the conjugated chain shows a decreased single-bond character, compared to the peripheral single bonds (1.469, 1.473 Å), in accordance with other molecules containing conjugated chains (*e.g.*, Stam & Riva di Sanseverino, 1966; Filippakis *et al.*, 1967). The bond and torsion angles (Table 6) of the central chain are affected mainly by the aromatic rings which form sterically hindered conjugated systems. The relaxation of the steric interactions near the phenyl ring is achieved by the opening of the bond angles at C(4) and C(7), (124.0, 126.9°) and a twist of 14.4° about C(4)-C(7), as observed in some chalcone derivatives (Rabinovich & Shakked, 1974). The non-bonded interactions near the dichlorophenyl ring are relaxed mainly by similar increase in the bond angles (125.9, 124.8°) at C(10) and C(11) and a large twist (40.8°) about C(10)-C(11). The significantly larger value (123.9°) of C(8)-C(9)-C(10) compared to that (121.2°) of the equivalent angle C(7)-C(8)-C(9) results also from these interactions by 'chain stretching'.

The minimum-energy geometry of the molecule in the gaseous and crystalline phases was calculated by means of a computer program (Warshel, 1974) based on the quantum mechanical extension of the Con-

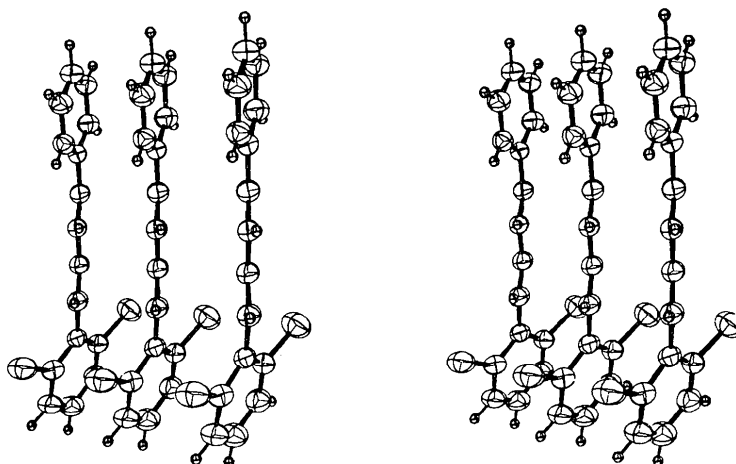


Fig. 4. Stereoscopic view of the molecules in the 4 Å translation stack. The view is edge-on along the plane of the butadiene.

Table 6. Selected bond lengths (Å), bond angles (°) and torsion angles (°) of the calculated and observed molecular geometry

The calculations were carried out by the QCFF/PI scheme (Warshel, 1974). The observed values are corrected for libration. A positive torsion angle corresponds to a right-handed screw (Klyne & Prelog, 1960).

Bond	Gas (calc.)	Crystal (calc.)	Crystal (obs.)
C(3)—C(4)	1.420	1.419	1.397
C(4)—C(5)	1.418	1.417	1.398
C(4)—C(7)	1.480	1.478	1.470
C(7)—C(8)	1.355	1.354	1.346
C(8)—C(9)	1.469	1.468	1.456
C(9)—C(10)	1.351	1.351	1.334
C(10)—C(11)	1.487	1.486	1.474
C(11)—C(12)	1.423	1.424	1.409
C(11)—C(16)	1.422	1.422	1.399
Bond angle			
C(3)—C(4)—C(7)	118.5	118.5	118.1
C(5)—C(4)—C(7)	122.9	122.8	124.0
C(4)—C(7)—C(8)	125.3	125.2	126.9
C(7)—C(8)—C(9)	120.7	120.6	121.2
C(8)—C(9)—C(10)	122.3	122.3	123.9
C(9)—C(10)—C(11)	123.5	123.7	125.9
C(10)—C(11)—C(12)	122.2	122.6	124.8
C(10)—C(11)—C(16)	119.1	119.0	120.6
C(11)—C(12)—C(26)	122.8	123.1	121.2
C(11)—C(16)—Cl(30)	121.7	121.9	119.4
Torsion angle			
C(5)—C(4)—C(7)—C(8)	-0.4	-15.1	-14.4
C(4)—C(7)—C(8)—C(9)	179.3	177.9	178.6
C(7)—C(8)—C(9)—C(10)	181.4	179.0	178.8
C(8)—C(9)—C(10)—C(11)	177.8	176.0	175.6
C(9)—C(10)—C(11)—C(12)	43.5	39.7	40.8
C(10)—C(11)—C(12)—Cl(26)	5.0	6.6	4.6
C(10)—C(11)—C(16)—Cl(30)	-0.3	-1.3	-0.6

sistent Force-Field to  $\pi$  electron system (Warshel & Karplus, 1972). The energy parameters used, involving C and H atoms were those of set A given by Warshel, Huller, Rabinovich & Shakked (1974) and the non-bonded potential parameters of Cl...Cl, Cl...C and Cl...H were the refined values of set B given by Bonadeo & D'Alessio (1973). Some of the calculated results are given in Table 6 together with the corresponding experimental values corrected for libration motion. The agreement between the observed and calculated values is fairly good, considering the approximations and assumptions introduced into the calculations on one hand, and the difficulty of correcting properly for librational motion, on the other. The relatively large deviations (2.5°) between the calculated and observed bond angles at C(11), C(12) and C(16) are due to the fact that no account was taken of the electron-withdrawing effects of the chlorine atoms in decreasing the *s*-character contribution to the related  $\sigma$ -bonds (Carter, McPhail & Sim, 1966). A comparison between the molecular geometry in the gaseous and the crystalline phase, leads to the conclusion that the twist about the single bond C(4)—C(7) results from crystal forces whereas the twist about C(10)—C(11) is due mainly to intramolecular forces.

### Molecular packing

Fig. 3 shows a stereoscopic view of the packing arrangement along [010]. The molecules pack in stacks along the short axis. The short intermolecular contacts are in the range of the quoted van der Waals distances (see Table 7). The shortest Cl...Cl contact (4.03 Å) is between atoms related by translation along the *b* axis, and is significantly longer than the sum of the van der Waals radii (3.6 Å). As stated above the 4 Å packing mode is a necessary topochemical condition for photocycloaddition reaction. This packing mode can be achieved with high degree of probability in aromatic compounds varying in size, symmetry and molecular weight, by introducing two chlorine atoms into a phenyl ring as shown by Green, Leser & Schmidt (1973). Similar effects were also observed in dibromo and diiodo compounds and are attributed to the dispersion energy gained by the interaction of two pairs of halogen atoms at this separation.

Table 7. Short intermolecular distances (Å)

The second atom in each pair is related to the first by the corresponding symmetry and translation operations.

	Symmetry element	Translation along			
		<i>a</i>	<i>b</i>	<i>c</i>	
C(1)...Cl(26)	2	0	1	0	3.67
C(3)...H(23)	2	-1	0	0	3.09
C(4)...C(5)	1	0	1	0	3.54
C(5)...H(22)	2	0	1	0	3.06
C(8)...H(19)	2	0	1	0	2.91
C(13)...H(27)	3	0	-1	0	2.89
C(14)...H(27)	3	0	-1	0	3.07
C(15)...H(29)	3	1	-1	0	3.04
H(17)...Cl(26)	2	0	0	0	3.18
H(17)...Cl(26)	2	0	1	0	3.20
H(17)...Cl(30)	2	-1	0	0	3.22
H(18)...Cl(30)	2	-1	1	0	3.09
H(21)...Cl(26)	2	0	0	0	3.24
H(28)...Cl(30)	3	1	0	0	3.23
H(29)...H(29)	3	1	0	0	2.46
H(29)...Cl(30)	3	1	0	0	3.17

Symmetry elements: (1)  $x, y, z$ ; (2)  $\frac{1}{2} + x, \frac{1}{2} - y, -z$ ; (3)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ .

### Photoreactivity

Fig. 4 presents a stereoscopic view of the molecules in the 4 Å translation stack, seen edge-on along the butadiene plane. This view demonstrates the steric effects of the dichlorophenyl groups which prevent close approach of adjacent molecules, and may explain the exclusive dimerization at the C=C double bond adjacent to the unsubstituted phenyl ring.

The contact geometry in the ground electronic state of any molecule with the adjacent molecules above it and below it along [010] is identical owing to translation symmetry. However, the excited molecule does not necessarily possess the same equilibrium geometry as in the ground state (Suzuki, 1967) and hence, any geometrical relaxation of such a non-planar molecule in the excited electronic state will lead to different ap-

proach configurations with its ground-state partner above and below, of which one may be more favourable for excimer formation (Cohen, Elgavi, Green, Ludmer & Schmidt, 1972) and subsequent dimerization. This behaviour is a necessary condition for creating unequal amounts of enantiomeric heterodimers in the two-component system (I and II) where the guest molecule (II), interleaved between two host molecules (I), is selectively excited as described earlier. An attempt is being made to study the preferred direction of photodimerization in this system by theoretical methods on one hand, and on the other by comparing the absolute configuration of the molecules in the initial mixed crystal with that of the heterodimer obtained in excess on irradiation of the same crystal.

### References

- BAVOUX, C. & THOZET, A. (1973). *Acta Cryst.* B29, 2603–2605.
- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* 8, 478–483.
- BERNSTEIN, J. (1972). *J. Chem. Soc. Perkin II*, pp. 946–949.
- BONADEO, H. & D'ALESSIO, E. (1973). *Chem. Phys. Lett.* 19, 117–119.
- CARTER, O. L., MCPHAIL, A. T. & SIM, G. A. (1966). *J. Chem. Soc. (A)*, pp. 822–827.
- COHEN, M. D., ELGAVI, A., GREEN, B. S., LUDMER, Z. & SCHMIDT, G. M. J. (1972). *J. Amer. Chem. Soc.* 94, 6776–6779.
- DAWSON, B. (1960). *Acta Cryst.* 13, 403–408.
- ELGAVI, A. (1973). Ph. D. Thesis. Weizmann Institute of Science.
- ELGAVI, A., GREEN, B. S. & SCHMIDT, G. M. J. (1973). *J. Amer. Chem. Soc.* 95, 2058–2059.
- FILIPPAKIS, S. E., LEISEROWITZ, L. & SCHMIDT, G. M. J. (1967). *J. Chem. Soc. (B)*, pp. 290–293.
- GREEN, B. S., LESER, J. & SCHMIDT, G. M. J. (1973). To be published.
- HAMILTON, W. C. (1965). *Acta Cryst.* 18, 502–510.
- HOPE, H. (1969). *Acta Cryst.* B25, 78–87.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* 21, 849–859.
- KAUFMAN, H. W. & LEISEROWITZ, L. (1970). *Acta Cryst.* B26, 442–443.
- KLYNE, W. & PRELOG, V. (1960). *Experientia*, 16, 521–523.
- LAHAV, M. (1968). Personal communication.
- MCWEENY, R. (1951). *Acta Cryst.* 4, 513–519.
- PALENIK, G. J., DONOHUE, J. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B24, 1139–1146.
- RABINOVICH, D. & SHAKKED, Z. (1974). *Acta Cryst.* B30, 2829–2834.
- SCHMIDT, G. M. J. (1967). *Reactivity of the Photoexcited Organic Molecule*, p. 227. New York: Interscience.
- SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B24, 63–67.
- STAM, C. H. & RIVA DI SANSEVERINO, L. (1966). *Acta Cryst.* 21, 132–138.
- SUZUKI, H. (1967). *Electronic Absorption Spectra and Geometry of Organic Molecules*, Chap. 5. New York: Academic Press.
- TROTTER, J. & WILLISTON, C. S. (1966). *Acta Cryst.* 21, 285–288.
- WARSHEL, A. (1974). *Program QCFF/PI for the Calculation of the Geometry of Conjugated Molecules in the Ground and Excited Electronic States*.
- WARSHEL, A., HULLER, E., RABINOVICH, D. & SHAKKED, Z. (1974). *J. Mol. Struct.* 23, 175–191.
- WARSHEL, A. & KARPLUS, M. (1972). *J. Amer. Chem. Soc.* 94, 5613–5625.