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Topochemistry. XI. The Crystal Structures of Methyl *m*- and *p*-Bromocinnamates

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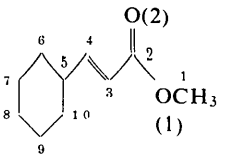
The packing arrangements of methyl *m*- and *p*-bromocinnamates have been determined from zonal and partly three-dimensional photographic data. The molecular shape of these esters, in particular the conformation of the $C_\beta-C_\alpha-C\begin{matrix}=O\\-O\end{matrix}$ system is discussed in terms of non-bonded interactions between C_β and the oxygen atoms of the carboxyl group, and compared with the configuration of this system in unsaturated and saturated acids and amides.

Introduction

In part III (Schmidt, 1964) of this series we have discussed the relationship between the photochemical behaviour of some ring-substituted cinnamic acids and their crystal structures. We have pointed out that these acids occur in three packing types (α, β, γ) with several acids crystallizing in more than one such type (dimorphism, trimorphism), that these packing types differ in the geometry of contact between neighbouring $>C=C<$ groups, and that the photochemical behaviour of the three types is explicable in terms of this geometry.

We have now begun an investigation of the crystal chemistry of the esters of cinnamic acids. The photochemistry of methyl cinnamate has been studied by Liebermann & Zsuffa (1911) and by de Jong (1923) who isolated small amounts of an oligomer ($n=3,4$) and the centric dimer (dimethyl α-truxillate) respectively. It would appear from the work of these authors that the ratio of the two products is temperature dependent, and that the yield of the dimer increases at lower temperatures; in view of the low melting point of methyl cinnamate (33°) the possibility could not be excluded that oligomerization takes place in the melt rather than in the crystalline state. In addition to this complication the cell dimensions of methyl cinnamate (Table 1) measured on a crystal grown by evaporation of an ether solution and photographed in a Lindemann capillary, are not suited to a structure analysis. Three heavy-atom derivatives of the ester were therefore prepared and their crystallographic constants determined (Table 1). The present paper presents the structure



(1)

Fig. 1. Numbering of atoms in the present analysis.

Table 1. *Crystallographic constants of some methyl cinnamates*

	a	*b*	*c*	β	Space group	*n*	d_{calc}
Methyl cinnamate	21·9	5·8	20·99	104°	$P2_1/c$	12	1·25
Methyl *p*-chlorocinnamate	8·77	5·84	18·75	95·6°	$P2_1/n$	4	1·37
Methyl *m*-bromocinnamate	7·830	5·976	21·208	99° 31′	$P2_1/a$	4	1·64
Methyl *p*-bromocinnamate	8·485	20·703	5·764	92·2°	$P2_1/n$	4	1·58

analyses of the methyl esters of *m*- and *p*-bromocinnamic acids; the results of the chemical study of the ultraviolet- and γ-irradiation products of these two compounds will be presented elsewhere.

Experimental

Methyl m-bromocinnamate

Methyl *m*-bromocinnamate, prepared by MeOH/HCl esterification of *m*-bromocinnamic acid, had m.p. 55–56°. Crystals grown from slowly cooled solutions in light petroleum (60–80°) are monoclinic needles elongated along [100], showing {001} and {011}. The intensities of the *h*0*l* and 0*kl* zones were collected from suitably shaped crystals with nickel-filtered Cu *K* radiation, and measured visually. No absorption corrections were applied. A trial model was established from the two Patterson projections $P(xz)$ and $P(yz)$ and refined by a combination of $(\varrho_o-\varrho_c)$ syntheses and of least-squares computations. The latter were based on the diagonal-approximation method (Rossmann, Jacobson, Hirshfeld & Lipscomb, 1959), which has been described, together with the weighting technique employed here, in part V of this series (Rabinovich & Schmidt, 1964). In the later least-squares cycles all the atoms except the methyl carbon were assigned anisotropic temperature factors; in addition, all but the methyl-group hydrogens were inserted on the basis of C–H bond lengths of 1·08 Å and normal bond angles, and kept fixed during the refinement. The refinement process was stopped when r $(=\Sigma w\ (k^2F_o^2-|F_c|^2)^2/\Sigma wk^4F_o^4)$ had reached 0·033, corresponding to R $(=\Sigma|kF_o-|F_c||)/\Sigma kF_o)$ of 0·066 for all reflexions excluding those for which $|F_c|<kF_{\text{threshold}}$.

Methyl p-bromocinnamate

Methyl *p*-bromocinnamate, prepared by MeOH/HCl esterification of *p*-bromocinnamic acid, had m.p. 96–97°. Crystals grown from ether solutions by evaporation are monoclinic needles elongated along [001], showing {010), {110} and {120}. The intensities of the *hk*0, *hk*1 and 0*kl* reflexions were collected from suitab-

Table 2. *Methyl m-bromocinnamate*

	Atomic coordinates (Å)			Thermal parameters (Å²)				
Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}
Br	1·542	1·134	1·052	0·0651	0·0413	0·0330	−0·0016	−0·0006
O(1)	4·610	−0·552	8·108	0·0739	0·0276	0·0461	−0·0013	−0·0007
O(2)	4·451	1·563	8·960	0·1027	0·0392	0·0404	−0·0017	−0·0127
C(1)	5·376	−0·954	9·376	0·0644*				
C(2)	4·205	0·796	8·044	0·0374	0·0239	0·0347	0·0117	−0·0012
C(3)	3·525	1·094	6·619	0·0565	0·0404	0·0406	−0·0014	0·0070
C(4)	3·058	2·268	6·324	0·0460	0·0472	0·0458	−0·0154	0·0059
C(5)	2·353	2·665	4·937	0·0475	0·0283	0·0408	0·0082	0·0133
C(6)	1·659	3·931	4·810	0·0654	0·0182	0·0528	−0·0073	0·0232
C(7)	0·978	4·410	3·588	0·0480	0·0389	0·0479	0·0039	0·0100
C(8)	0·929	3·526	2·399	0·0522	0·0237	0·0429	0·0211	0·0088
C(9)	1·585	2·263	2·536	0·0433	0·0125	0·0345	−0·0031	0·0107
C(10)	2·324	1·881	3·807	0·0433	0·0311	0·0284	0·0009	0·0009
				U*				
H(3)	3·36	0·44	5·91	0·076				
H(4)	3·18	3·01	7·12	0·076				
H(6)	1·62	4·46	5·60	0·076				
H(7)	0·42	5·17	3·47	0·076				
H(8)	0·44	3·78	1·57	0·076				
H(10)	2·79	1·10	3·90	0·076				

* Isotropic thermal parameters.

Table 3. *Methyl p-bromocinnamate*

	Atomic coordinates (Å)			Thermal parameter (Å²)					
	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Br	−0·775	4·872	0·107	0·1195	0·0785	0·0991	−0·0231	−0·0100	−0·0205
O(1)	2·143	11·577	6·030	0·0651	0·0926	0·0612	−0·0127	−0·0356	0·0158
O(2)	3·579	11·514	4·408	0·0749	0·1323	0·1079	−0·0488	−0·0754	0·0506
C(1)	3·020	12·582	6·653	0·0949	0·1083	0·0886	−0·0255	−0·0214	−0·0109
C(2)	2·572	11·141	4·881	0·0564	0·0683	0·1202	0·0079	0·0097	0·0115
C(3)	1·664	10·091	4·223	0·0549	0·0623	0·0804	0·0060	−0·0104	−0·0030
C(4)	2·002	9·486	3·169	0·0558	0·0744	0·0636	0·0068	0·0037	0·0106
C(5)	1·287	8·423	2·481	0·0507	0·0555	0·0553	−0·0016	0·0128	0·0050
C(6)	1·768	7·908	1·237	0·0699	0·0688	0·0587	−0·0043	−0·0004	0·0181
C(7)	1·196	6·863	0·529	0·0729	0·0607	0·0554	0·0025	0·0066	0·0051
C(8)	0·044	6·321	1·058	0·0605	0·0608	0·0474	0·0002	0·0034	−0·0063
C(9)	−0·489	6·786	2·194	0·0596	0·0760	0·0585	−0·0146	0·0080	−0·0014
C(10)	0·121	7·815	2·886	0·0589	0·0750	0·0726	−0·0040	0·0065	−0·0040

ly shaped crystals with nickel-filtered Cu K radiation and measured visually. Only the extended spots of the $hk1$ films were read, and corrected for spot extension by the method due to Phillips (1956). No absorption corrections were applied. The trial model deduced from the two Patterson projections $P(xy)$ and $P(yz)$ was refined by means of a modified Busing & Levy least-squares program. All atoms were treated anisotropically; no hydrogen atoms were included at any stage of the refinement. The final agreement factors after 5 cycles of refinement were $r=0{\cdot}047$ and $R=0{\cdot}101$.

The scattering factor curves used in both structure analyses were: $f_{C,O}$, Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955); f_{Br}, *In-*

Table 4. *List of observed and calculated structure factors. Methyl m-bromocinnamate**

0 0 2	3713	3668		22	1056	916		-8	8418	8754		-13	4517	-4423									
3	4103	5003		23	978	691		-9	6348	6257		-14	2547	-2578									
4	2735	-2487		24	1056	1023		-10	8081	8417		-15	1631	-1631									
5	4066	3977	0 4 1		<326	320		-11	4742	4526		-16	1243	-1132									
6	5572	-6232	2		978	979		-12	3000	3323		-17	853	-890									
7	3162	-3277	3		804	-747		-13	465	425		-18	476	-486									
8	7358	-8407	4		1731	1724		-14	2158	-1802		-19	<351	-95									
9	6964	-8176	5		1517	1167		-15	3927	-3962		-20	<325	336									
10	6576	-6392	6		<339	289		-16	3790	-3822		-21	1104	1164									
11	7742	-8742	7		741	607		-17	6624	-6854		-22	1266	1393									
12	7579	-7730	8		2296	-2494		-18	6285	-6332		-23	639	653									
13	3100	-2950	9		765	-722		-19	653	-449		-24	967	1086									
14	3852	-3922	10		1368	-1320		-20	2208	-2231		8 0 0	1970	-2143									
15	3990	-3747	11		<376	-203		-21	1417	-1526		1	816	-974									
16	4229	4106	12		2911	2624		-22	1494	-1569		2	302	-539									
17	4466	4323	13		1155	-1156		-23	1289	-1139		3	<302	-18									
18	5082	5158	14		527	476		-24	1255	1053		4	<365	311									
19	4041	4074	15		<365	-55		-25	904	877		5	<351	351									
20	2247	2038	16		1306	-1209		-26	1782	1875		6	1117	1086									
21	3501	3675	17		351	107		-27	1317	1599		7	1280	1220									
22	2221	2400	18		904	-732		4 0 0	<239	281		8	1329	1269									
23	2358	2264	19		753	557		1	3037	2808		9	1317	1192									
24	1329	1137	20		<276	387		2	6262	6211		10	1857	1793									
25	<263	-439	21		<251	281		3	5207	4810		11	978	1092									
26	<439	371	22		576	644		4	9673	10147		12	439	543									
0 2 0	8332*	-12129	0 5 1		866	753		5	7779	7498		-1	1368	-1247									
4	2409	-2322	2		1455	1385		6	1443	1654		-2	1631	-1909									
6	1543	1405	3		2133	1911		7	4192	4131		-3	1768	-1748									
0 1 1	6136	-6127	4		2786	2532		8	1819	1515		-4	1443	-1469									
2	3325	-3334	5		1217	-1208		9	1355	1187		-5	1280	-1214									
3	6850*	-9448	6		1217	821		10	<302	-84		-6	<314	423									
4	9234*	-12196	7		1745	1446		11	2547	-2533		-7	790	745									
5	7979*	-9756	8		1706	1475		12	3148	-3429		-8	841	942									
6	7064	-7618	9		<376	181		13	4466	-4436		-9	527	391									
7	7516	-8593	10		1768	-1815		14	4103	-4062		-10	678	819									
8	7277	-7509	11		1066	1070		15	3211	-3241		-11	1657	1567									
9	1317	695	12		<365	-276		16	2498	-2505		-12	1668	1501									
10	2107	-1745	13		553	-334		17	2547	-2745		-13	1229	1015									
11	1480	1279	14		1117	-857		18	1292	-1210		-14	1368	1193									
12	4366	3860	15		2435	-2168		19	1166	-1047		-15	539	602									
13	4780	4774	16		853	-475		20	690	793		-16	<288	-264									
14	6387	6521	17		527	-470		21	1819	1839		-17	<263	81									
15	5672	5661	18		816	-573		22	978	1159		-18	<239	-335									
16	6097	6054	19		<214	-0		-1	< 225	47		-19	451	-480									
17	2158	1861	20		490	424		-2	4568	-3936													
18	2723	2631	0 6 1		1794	1910		-3	3280	-3024													
19	2284	1925	2		1092	1011		-4	7491	-6870													
20	<376	57	3		1078	1200		-5	6174	-6286													
21	<365	-179	4		1731	1756		-6	3613	-3236													
22	1908	-1977	5		439	-6		-7	9259	-8911													
23	2184	-1903	6		<351	-26		-8	3100	-2890													
24	3037	-2789	7		1392	-1472		-9	1811	-1875													
25	2247	-1943	8		2033	-2195		-10	4605	-4443													
26	1682	-1712	9		1392	-1354		-11	916	-896													
0 2 1	5044	-5541	10		2082	-1868		-12	2247	1948													
2	5721	-5947	11		1719	-1701		-13	4166	4223													
3	2233	-2260	12		1217	-1079		-14	4291	4201													
4	2170	-1594	13		653	-218		-15	4115	4341													
5	2849	-2353	14		<239	-338		-16	3550	3606													
6	1180	611	15		<214	262		-17	3137	3122													
7	778	728	0 7 1		929	-863		-18	2070	2149													
8	8857	9361	2		1192	-1277		-19	1706	1771													
9	6023	5916	3		1029	-1147		-20	502	-537													
10	5595	5435	4		1380	-1589		-21	<302	-262													
11	5031	4956	5		1104	-1165		-22	1092	1040													
12	1882	1938	6		1745	-1977		-23	1494	-1556													
13	4027	3653	7		1417	-1715		-24	1392	-1398													
14	1306	1254	2 0 0		9034	-9341		-25	1557	-1589													
15	1078	864	1		11581*	-17541		-26	1557	-1727													
16	1431	-1321	2		7916	-8412		6 0 0	853	906													
17	2196	-2127	3		10690*	-12687		1	1506	1270													
18	1996	-1949	4		6738	-7279		2	665	711													
19	3162	-3100	5		5583	-5492		3	3225	-3350													
20	1996	-1862	6		3839	-3940		4	2647	-2381													
21	1831	-1870	7		4554	4513		5	3852	-3789													
22	2484	-2134	8		1355	1161		6	3299	-2990													
23	1970	-1897	9		678	486		7	2521	-2496													
24	827	-807	10		7352	7165		8	2772	-2824													
25	<214	230	11		6411	6276		9	1870	-2015													
0 3 1	1016	921	12		5634	5151		10	2059	-2135													
2	527	-498	13		7477	6956		11	716	-656													
3	6450	6399	14		5432	5321		12	576	640													
4	2059	1968	15		4654	4309		13	2270	2078													
5	3776	3523	16		2284	2386		14	1643	1562													
6	3941	3540	17		702	-685		15	1857	1735													
7	1745	1307	18		866	-889		16	1619	1586													
8	2170	2174	19		2208	-2259		17	1894	1671													
9	<314	-210	20		2709	-2890		18	1808	2017													
10	878	762	21		2849	-2557		-1	2672	2755													
11	639	-530	22		4015	-3764		-2	2435	2123													
12	827	-606	23		1808	-1740		-3	3690	3699													
13	1389	-1326	24		1406	-1580		-4	4742	4488													
14	2623	-2554	25		1619	-1805		-5	4266	4138													
15	2321	-2137	-1		7477	-8207		-6	2735	2471													
16	1506	-1418	-2		<151	-282		-7	314	497													
17	1266	-961	-3		12684*	16290		-8	702	539													
18	1845	-1890	-4		6299	-5933		-9	451	630													
19	565	-506	-5		4993	4694		-10	1531	-1436													
20	339	-42	-6		9148	9720		-11	1029	-971													
21	<314	266	-7		5370	5562		-12	2247	-2341													

* Columns are in the order h, k, l, $100F_o$, $100F_c$.

ternational Tables for X-Ray Crystallography (1962), f_H, McWeeny (1951).

Discussion

The molecular dimensions (Fig. 2) based on the last least-squares cycles are to be regarded as approximate only; better values would certainly require further experimental data. Since we have aimed at determining the packing arrangement only, we have made no effort to improve on the present admittedly incomplete refinement; in particular, overlap in the (100) projection in the *m*-derivative has caused difficulties in the accurate positioning of the carboxyl oxygen and of the ring-carbon 7. The positional and thermal parameters

Table 5. *List of observed and calculated structure factors. Methyl p-bromocinnamate**

1 1 0	12.47	-10.52		5.42	3.69		5.09	4.09		6.07	6.05								
2	16.41	17.57	5 1 0	22.65	-23.46	1 0 1	61.06	70.52		4.43	4.69								
3	44.48	42.72	2	10.34	-9.70	1	32.50	29.85		2.79	-2.98								
4	49.24	-50.49	3	16.91	14.38	2	70.41*	-86.93	5 0 1	33.48	-33.87								
5	15.59	19.28	4	10.18	-10.18	3	33.48	25.97	1	9.52	9.11								
6	<1.81	-1.08	5	11.32	-10.34	4	110.13*	162.79	2	32.66	31.34								
7	63.03	-67.43	6	<3.12	-2.40	5	97.00*	133.54	3	10.83	-9.22								
8	27.25	-30.09	7	19.70	19.67	6	35.62	-41.57	4	40.87	-39.19								
9	44.81	40.61	8	16.25	-15.30	7	23.47	-22.32	5	25.93	24.03								
10	47.76	41.00	9	30.86	-30.36	8	26.26	28.51	6	34.14	31.24								
11	70.74	-66.13	10	27.08	26.25	9	53.83	45.07	7	11.65	10.90								
12	<2.79	-6.78	11	16.74	15.99	10	51.86	-44.29	8	31.35	-30.13								
13	49.89	42.51	12	5.09	-5.30	11	21.83	-21.40	9	18.22	18.69								
14	32.83	33.92	13	13.13	-14.07	12	24.78	24.73	10	20.35	21.34								
15	33.15	-30.68	14	<3.61	.48	13	5.09	-5.07	11	2.63	-1.96								
16	15.10	-14.79	15	6.40	6.43	14	1.97	1.40	12	4.76	-5.04								
17	21.17	20.93	16	<3.61	-2.01	15	8.04	-7.95	13	4.27	-3.75								
18	14.12	14.35	17	15.43	-15.91	16	<2.13	-.18	14	4.10	4.68								
19	15.59	-13.53	18	<3.45	1.95	17	<2.13	.04	15	6.07	6.83								
20	8.04	-8.69	19	12.47	9.07	18	<2.13	-1.47	16	5.58	-6.50								
21	14.94	12.49	20	<2.95	-2.56	19	4.76	-5.64	17	7.22	-7.74								
22	6.73	5.57	21	7.71	-6.29	20	4.76	-4.09	18	<1.97	2.41								
23	8.70	-7.59	22	<2.30	-.14	21	<1.97	.06	19	7.22	6.99								
24	<2.79	-2.22	23	6.89	6.17	22	7.06	5.08	20	2.13	1.55								
25	<2.46	2.75	6 0 0	22.32	-24.25	23	2.46	3.30	21	6.07	4.89								
26	5.58	4.80	1	8.70	-6.29	24	6.07	-5.77	22	<1.64	-1.34								
2 0 0	8.21	7.41	2	13.46	14.19	25	<1.64	-.47	23	2.79	2.65								
1	56.62	53.63	3	3.28	1.31	26	4.27	4.25	6 1 1	2.46	2.13								
2	122.60	113.71	4	31.35	-30.35	2 1 1	45.14	44.72	2	<1.97	1.39								
3	144.95*	158.85	5	21.34	-18.76	2	43.17	40.56	3	10.34	9.89								
4	17.23	17.06	6	23.31	23.21	3	35.78	-31.84	4	3.94	-4.55								
5	63.52	56.02	7	4.92	3.57	4	60.89	-49.91	5	31.51	-29.05								
6	15.59	-10.68	8	<3.61	-1.74	5	1.31	-1.24	6	7.71	7.96								
7	63.19	-59.21	9	21.50	-21.50	6	72.38	70.92	7	9.36	8.59								
8	16.25	13.44	10	23.14	24.48	7	48.58	-40.22	8	2.95	-3.66								
9	44.97	41.86	11	<3.61	-3.03	8	9.19	-11.56	9	9.52	-9.22								
10	<2.63	2.11	12	<3.61	-4.10	9	9.86	8.83	10	<2.13	-1.24								
11	34.63	-36.60	13	<3.61	-.04	10	25.77	26.86	11	8.70	8.46								
12	8.86	7.84	14	<3.61	-1.32	11	42.67	-39.79	12	3.45	3.84								
13	10.34	10.78	15	9.36	8.15	12	34.96	-31.66	13	19.37	-18.10								
14	<3.28	2.24	16	<3.45	-.95	13	24.29	20.43	14	<2.13	-1.17								
15	4.76	-4.91	17	8.70	-5.20	14	27.74	25.81	15	14.77	13.46								
16	<3.61	1.56	18	7.55	-4.94	15	16.74	-14.58	16	<1.97	1.83								
17	6.24	6.17	19	3.94	3.55	16	26.42	-28.04	17	10.18	-9.05								
18	<3.61	.58	20	3.61	2.41	17	22.65	21.20	18	5.09	-5.39								
19	<3.61	1.35	7 1 0	5.09	-6.14	18	21.50	21.66	19	7.88	6.57								
20	6.24	-5.78	2	<3.61	3.48	19	8.70	-8.05	20	<1.64	-1.99								
21	<3.45	-4.09	3	7.22	5.94	20	9.19	-9.54	21	3.94	-3.72								
22	<3.28	3.37	4	8.04	7.91	21	<1.97	.74	7 0 1	6.73	-7.11								
23	<2.95	2.90	5	6.24	-6.29	22	10.85	10.56	1	17.56	-17.14								
24	4.60	-3.83	6	8.21	-7.19	23	<2.13	-1.80	2	12.21	13.95								
25	5.91	-4.95	7	13.62	14.09	24	5.09	-5.14	3	5.91	6.11								
3 1 0	<1.97	3.17	8	<3.61	-1.13	25	<1.48	1.65	4	<2.13	.86								
2	4.10	1.62	9	<3.61	-2.95	3 0 1	16.25	13.96	5	22.98	-21.37								
3	16.91	17.32	10	7.22	-7.03	1	70.74	67.88	6	20.02	20.18								
4	36.44	-31.61	11	8.04	8.14	2	15.26	18.57	7	<2.13	-1.38								
5	4.60	-2.09	12	3.61	3.83	3	73.53	-72.26	8	10.83	-12.21								
6	40.70	35.58	13	4.92	-3.80	4	4.60	-4.76	9	4.76	-5.79								
7	7.06	8.34	14	5.74	-5.03	5	31.35	33.72	10	4.27	-3.66								
8	50.88	-47.17	15	4.60	5.12	6	21.17	-17.92	11	7.39	7.60								
9	<2.79	-.19	16	10.83	8.16	7	102.25	102.63	12	<1.97	-.11								
10	33.32	34.28	17	<2.79	-1.36	8	22.81	-23.99	13	4.43	-4.86								
11	8.53	10.24	18	<2.46	-1.10	9	35.94	34.86	14	3.61	-4.06								
12	41.05	-41.96	19	<2.13	2.73	10	4.60	5.15	15	4.60	5.03								
13	12.80	11.21	20	7.39	5.71	11	16.41	-15.42	16	2.13	1.09								
14	30.53	30.72	8 0 0	<3.61	1.00	12	13.29	-13.75	17	<1.97	-2.21								
15	3.61	-2.89	1	11.65	-10.94	13	16.41	15.41	18	2.46	-1.37								
16	21.66	-21.01	2	<3.61	-1.82	14	8.70	8.64	19	3.12	2.84								
17	<3.61	-3.89	3	11.49	9.53	15	4.92	-3.69	8 1 1	<2.13	-1.24								
18	17.89	16.91	4	3.61	-4.57	16	6.24	-6.28	2	4.76	5.55								
19	5.09	5.70	5	<3.61	-1.97	17	4.10	-4.18	3	4.43	5.65								
20	14.77	-13.79	6	6.24	4.55	18	5.09	5.67	4	3.94	-4.25								
21	<3.28	-3.49	7	11.82	11.49	19	4.43	3.43	5	<2.13	-2.34								
22	10.18	8.02	8	<3.45	-2.00	20	<1.97	-.04	6	3.28	-1.72								
23	3.94	3.91	9	<3.45	-1.88	21	4.76	-4.15	7	4.43	5.58								
24	6.40	-5.10	10	<3.45	-.08	22	4.76	4.55	8	4.92	5.19								
25	2.63	-3.31	11	5.74	3.05	23	3.94	3.44	9	<1.97	.10								
4 0 0	19.04	-17.02	12	<3.12	1.06	24	3.61	-3.17	10	8.86	-6.78								
1	60.89	64.92	13	4.27	-4.88	25	3.61	-3.56	11	<2.30	1.36								
2	54.33	51.40	9 1 0	<3.45	-1.69	4 1 1	3.94	3.20	12	7.88	6.47								
3	29.71	-29.04	2	<3.28	2.56	2	15.92	13.39	13	2.30	-3.29								
4	25.77	-23.40	3	<3.28	-.32	3	14.44	14.79	14	3.94	-3.36								
5	26.75	28.07	4	<3.28	2.39	4	34.96	-33.51	15	<1.81	-.03								
6	35.29	36.85	5	<3.28	-.51	5	<1.64	-.34	16	7.22	7.13								
7	23.80	-20.12	6	<3.12	-.77	6	26.92	24.67	17	3.28	-3.56								
8	30.36	-30.20	7	<3.12	-.60	7	25.44	24.90	9 1 1	2.95	-3.60								
9	23.47	23.29	8	5.25	4.74	8	41.36	-36.37	2	7.71	-7.19								
10	13.79	13.35	9	<2.95	-1.26	9	7.88	-8.39	3	10.83	9.83								
11	<3.28	-.64	10	4.76	-3.99	10	33.32	27.14	4	<2.30	-.79								
12	34.30	-33.95	11	<2.63	2.61	11	7.71	7.91	5	2.63	-2.93								
13	15.59	16.38	12	<2.46	2.20	12	17.73	-15.38	6	3.94	-2.63								
14	8.70	9.00	13	6.57	4.05	13	12.31	-14.16	7	<2.13	.33								
15	<3.61	1.17	14	3.28	-2.70	14	21.50	20.62	8	2.95	2.20								
16	5.25	3.20	10 1 0	<2.63	-3.32	15	12.31	13.07	9	2.95	-2.43								
17	8.21	-7.15	2	<2.63	-1.67	16	16.58	-14.59	10	<1.81	.08								
18	<3.61	1.24	3	<2.63	.50	17	5.25	-6.04	11	<1.81	.07								
19	6.89	6.53	4	5.09	3.76	18	11.82	10.83	12	3.28	3.40								
20	<3.28	-.87	5	<2.46	1.12	19	7.55	8.86	13	1.48	.21								
21	6.24	-5.41	6	<2.30	-.34	20	12.64	-10.21	-1 0 1	52.69	48.84								
22	<2.79	-.48	7	<2.30	.43	21	5.58	-7.14	1	79.95*	120.75								

* Columns are in the order h, k, l, $100\,F_o$, $100\,F_c$.

Table 5 (*cont.*)*

2		97.64*	135.43	-5	0	1	66.47	-71.20		8		40.21	35.95			15		2.63	-3.27
3		22.98	25.33			1	12.80	-15.60		10		47.76	-48.01			16		9.03	8.42
4		43.17	42.81			2	25.44	24.29		12		13.29	12.48			17		3.45	3.57
5		58.76*	-70.39			3	5.74	-5.34		14		37.26	-31.89			18		<2.79	-.38
6		62.04	-68.79			4	28.56	-26.03		16		8.37	9.17			19		3.77	-4.16
7		42.94	42.14			5	8.53	-10.47		18		10.01	10.07			20		<2.30	-1.59
8		43.00	41.54			6	27.25	24.93		20		<2.63	-4.57			21		3.12	3.66
9		17.73	-16.69			7	6.24	-5.51		22		5.58	6.00	0	1	5		<2.63	-1.92
10		21.99	-19.49			8	20.35	-18.47		24		<2.63	-1.95			2		2.79	-2.32
11		9.36	9.80			9	4.27	2.88		26		3.94	3.81			3		<2.79	-.72
12		22.65	20.34			10	19.04	19.51	0	1	1	7.06	7.02			4		2.79	3.55
13		12.15	-12.81			11	2.46	2.38		2		51.21	53.35			5		6.40	6.35
14		6.73	-6.46			12	7.55	-7.63		3		32.99	-37.67			6		16.08	-16.55
15		10.83	11.23			13	17.73	18.43		4		11.49	-9.67			7		<2.79	-1.53
16		<2.13	3.65			14	11.98	11.99		5		33.48	31.08			8		<2.79	-1.54
17		3.28	2.44			15	4.60	5.45		6		14.61	9.66			9		5.74	6.72
18		4.27	4.11			16	<2.13	.57		7		43.00	-38.72			10		8.21	-7.44
19		4.60	4.55			17	<1.97	2.05		8		12.64	13.07			11		8.86	-9.23
20		2.95	-2.93			18	2.79	-3.26		9		79.11	72.93			12		7.06	5.84
21		1.97	2.83			19	5.58	-5.03		10		22.16	-22.00			13		10.34	9.72
22		<2.30	1.05			20	2.13	1.58		11		50.22	-44.34			14		<2.95	-2.38
23		4.27	-4.06			21	<1.81	1.49		12		7.39	7.31			15		4.76	-5.38
24		5.09	-4.54			22	3.77	-3.53		13		45.14	44.21			16		2.63	3.58
25		2.30	2.34			23	<1.31	-.21		14		14.94	-14.21			17		6.24	5.52
26		2.95	2.97	-6	1	1	<1.97	.98		15		45.14	-39.18			18		2.30	-2.47
-2	1	1	18.87	9.50			2	<1.97	.28		16		5.58	-3.22			19		8.28	-3.33
	2		28.72	-16.43			3	8.70	8.56		17		23.80	22.84	0	0	6		5.42	4.02
	3		31.51	-25.90			4	8.37	-8.11		18		3.28	-3.37			1		8.70	-8.46
	4		46.45	44.41			5	13.62	-13.91		19		21.17	-21.72			2		9.03	-9.03
	5		6.24	6.60			6	2.46	.78		20		2.63	-1.13			3		6.40	5.88
	6		10.67	-11.48			7	10.83	9.23		21		13.29	14.37			4		6.89	5.48
	7		1.31	1.69			8	3.94	-3.27		22		3.94	-3.89			5		<3.12	-1.53
	8		33.15	32.06			9	11.65	-10.82		23		4.27	-4.99			6		7.55	-5.84
	9		28.72	24.05			10	4.76	3.23		24		<2.46	-1.66			7		2.95	1.09
	10		47.93	-47.15			11	20.68	18.62		25		3.28	4.67			8		6.40	5.32
	11		12.47	-11.56			12	3.45	-1.56	0	0	2	84.53	84.38			9		3.94	-4.07
	12		38.24	37.69			13	2.13	-1.07		1		18.71	-21.61			10		2.63	-.67
	13		17.07	15.42			14	2.95	.93		2		96.34	-87.78						
	14		34.47	-32.97			15	12.47	12.34		3		28.23	32.72						
	15		6.24	-5.19			16	1.97	-3.08		4		63.03	58.67						
	16		35.12	34.79			17	5.74	-4.87		5		20.68	-21.09						
	17		16.74	14.92			18	<2.13	1.33		6		74.02	-73.19						
	18		17.73	-18.08			19	4.43	4.58		7		14.94	-15.44						
	19		4.92	-5.23			20	3.94	-3.44		8		38.24	38.81						
	20		9.85	10.60			21	2.95	-2.75		9		20.35	-20.77						
	21		<1.97	-1.86	7	0	1	5.58	-7.36		10		46.78	-43.47						
	22		<2.30	-2.56			1	11.49	9.28		11		5.25	-5.16						
	23		<2.13	-2.30			2	2.63	3.31		12		21.01	21.91						
	24		7.55	7.43			3	16.58	-13.72		13		2.95	3.22						
	25		<1.48	-.52			4	2.13	-3.76		14		11.66	-10.17						
-3	0	1	30.44	-30.76			5	8.86	7.08		15		<2.63	1.46						
	1		54.49	-54.10			6	6.24	8.12		16		<2.63	-.59						
	2		31.84	34.28			7	10.18	-9.50		17		<2.79	2.03						
	3		87.97*	96.64			8	9.19	-10.29		18		<2.79	2.18						
	4		5.42	5.18			9	6.73	6.68		19		<2.63	-.46						
	5		54.98	-49.97			10	4.27	-3.84		20		4.10	-4.42						
	6		9.03	10.56			11	9.85	-9.41		21		2.95	3.39						
	7		49.57	46.06			12	<2.13	.23		22		6.24	5.88						
	8		7.39	-7.93			13	<1.97	1.43		23		<2.46	.97						
	9		30.69	-29.06			14	<1.97	-1.66		24		<2.13	-1.51						
	10		29.87	27.15			15	4.43	-4.03		25		<1.81	2.16						
	11		4.92	5.47			16	<2.13	2.11	0	1	3	28.39	25.85						
	12		5.91	-6.77			17	<1.97	.92		2		9.03	-9.02						
	13		11.98	-11.71			18	<1.81	-.93		3		22.49	-22.52						
	14		4.27	4.88			19	<1.48	1.72		4		16.74	-16.90						
	15		4.10	-4.04			20	1.97	2.07		5		19.20	16.39						
	16		15.10	-15.27	-8	1	1	<2.13	1.98		6		20.63	-22.44						
	17		8.04	-8.28			2	<2.13	-.04		7		22.98	-22.19						
	18		4.76	-4.84			3	<2.13	3.59		8		11.98	13.31						
	19		<2.13	.15			4	5.42	-5.38		9		38.73	36.69						
	20		4.27	4.77			5	5.74	-6.71		10		19.20	-19.44						
	21		4.10	3.24			6	<2.13	-.98		11		34.14	-33.46						
	22		4.43	4.12			7	<2.13	1.76		12		22.16	21.75						
	23		5.25	-5.34			8	9.68	-9.55		13		7.22	5.13						
	24		<1.64	-1.27			9	2.79	1.67		14		10.01	10.79						
	25		3.94	4.00			10	6.73	5.07		15		24.78	-22.74						
-4	1	1	11.00	-10.80			11	5.74	-4.51		16		8.70	9.10						
	2		8.53	-8.13			12	2.63	-1.32		17		11.32	12.10						
	3		21.83	-21.20			13	4.92	-5.07		18		3.28	-4.42						
	4		1.48	2.15			14	6.24	6.02		19		12.31	-10.64						
	5		16.91	-14.78			15	<1.81	.26		20		<2.95	2.54						
	6		28.23	-28.46			16	<1.64	1.85		21		8.70	9.03						
	7		41.03	36.92	-9	0	1	12.97	9.67		22		<2.46	-2.91						
	8		18.38	16.00			1	<2.30	1.10		23		3.77	-4.08						
	9		16.41	-14.24			2	<2.30	.01		24		1.81	3.17						
	10		5.58	-6.33			3	8.86	-7.35	0	0	4	37.09	36.76						
	11		13.13	14.94			4	4.60	3.00		1		5.91	-7.05						
	12		26.10	24.70			5	<2.30	.31		2		16.25	-17.16						
	13		26.10	-24.88			6	2.30	-1.23		3		22.32	22.31						
	14		24.62	-23.50			7	<2.13	.05		4		30.36	28.49						
	15		2.13	2.42			8	<2.13	-1.38		5		5.25	-4.87						
	16		11.49	12.24			9	<1.97	1.18		6		32.00	-32.67						
	17		7.88	-8.14			10	<1.97	-.45		7		11.00	10.27						
	18		6.40	-6.48			11	1.31	-2.63		8		22.98	21.62						
	19		6.73	6.73			12	5.09	4.64		9		7.98	-8.32						
	20		5.25	4.41			13	2.63	2.61		10		14.94	-13.76						
	21		9.85	-9.69			14	<1.31	-1.20		11		6.57	6.70						
	22		2.95	-3.40	0	2	0	44.48	-50.40		12		2.79	3.85						
	23		6.89	7.19			4	63.85*	77.90		13		<2.79	-3.66						
	24		<1.31	-1.68			6	97.48	-89.43		14		<2.63	2.29						

* Columns are in the order h, k, l, $100F_o$, $100F_c$.

of the last refinement cycles are given in Tables 2 and 3. Packing diagrams are shown in Figs. 3 and 4. Structure factors are listed in Tables 4 and 5, where reflexions believed to suffer from secondary extinction and hence assigned zero weight in the least-squares refinement are asterisked while the unobserved reflexions are marked $<kF_o$. Close intermolecular contacts, arbitrarily bounded at the sums of the van der Waals radii (Pauling, 1960) plus 0·2 Å, are listed in Tables 6 and 7.

Molecular shape.

The equations of the best planes through the benzene ring C(5)–C(10), the ethylenic group C(2)C(3) C(4)C(5) and the group C(2)C(3)O(1)O(2), computed

Table 6. *Methyl m-bromocinnamate*

Intermolecular contacts (Å) between molecule at (*xyz*) and its nearest neighbour related by

1. *a*-glide plane
   Br · · · Br = 3·98
   Br · · · C(8) = 3·75
   C(5) · · · C(7) = 3·60
   C(3) · · · C(6) = 3·58
   C(3) · · · C(5) = 3·53
   C(3) · · · C(4) = 3·53
   C(1) · · · C(1) = 4·06

2. twofold screw axis
   C(1) · · · C(1) = 3·98
   C(1) · · · O(2) = 3·21

3. inversion centre at (000)
   Br · · · Br = 4·12

Table 7. *Methyl p-bromocinnamate*

Intermolecular contacts (in Å) between molecule at (*xyz*) and its nearest neighbour related by

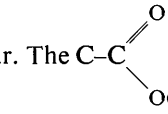
1. *n*-glide plane
   C(5) · · · Br = 3·68
   C(6) · · · Br = 3·41
   C(7) · · · Br = 3·56

2. twofold screw axis
   Br · · · C(1) = 3·77

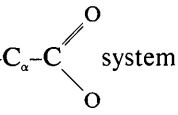
3. inversion centre at $(0\frac{1}{2}\frac{1}{2})$
   C(1) · · · C(10) = 3·79
   C(3) · · · C(10) = 3·55

4. inversion centre at $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$
   O(2) · · · C(6) = 3·39

5. translation along *c*
   C(3) · · · C(6) = 3·53

according to Schomaker, Waser, Marsh & Bergman (1959) are listed, together with the deviations of atoms from their planes, in Tables 8 and 9. In both compounds the benzene rings and the ethylenic systems may be regarded as planar. The  system is planar in the *p*-derivative; in the *m*-compound the CH_3 group is displaced by 0·1 Å from the plane of ($C–CO_2$). This deviation from planarity cannot be accounted for in terms of intermolecular contacts: the distances between CH_3 and its two nearest neighbours (Table 6) do not change significantly when the methyl group is moved into the plane of ($C–CO_2$).

At the outset of these structure determinations we held to the view that the $>C=O$ bond of the carboxyl group would adopt the *trans* configuration with respect to the $>C=C<$ bond which had been found in *trans*-cinnamic acid (Ladell, McDonald & Schmidt, unpublished). In fact, the *cis* arrangement is adopted by both *p*- and *m*-bromocinnamates.

We may assume that, as a first approximation, the conformation of the  system is determined by the non-bonded interaction between C(4) and its hydrogen, H(4), on the one hand and the 'ether' and 'carbonyl' oxygen atoms O(1) and O(2) on the other hand. Since the C(3)–C(2)=O(2) angle is larger than the C(3)–C(2)–O(1) angle greater C(4) · · · O and H(4) · · · O separation will be achieved if C(4)–H(4) lies opposite the 'carbonyl' oxygen atom, *i.e.* if the

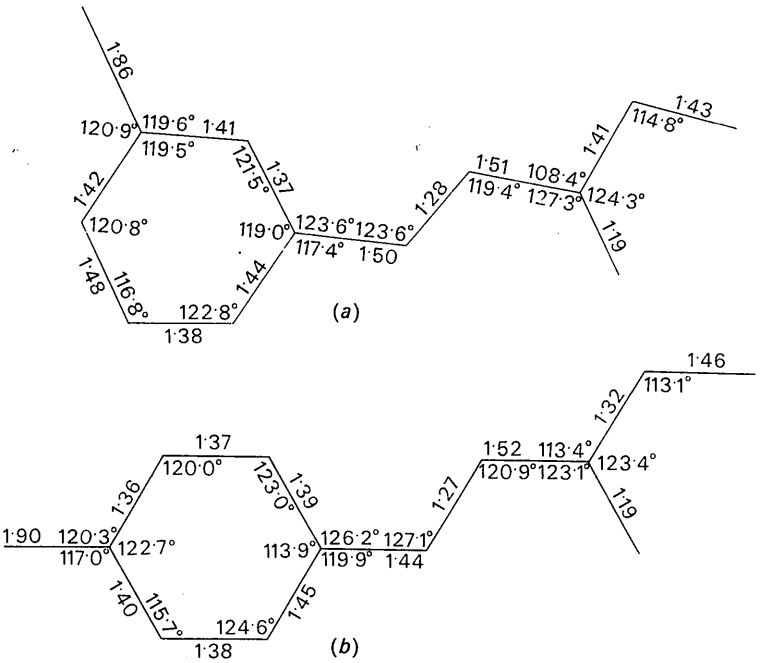


Fig. 2. Experimental bond lengths and angles. (*a*) Methyl *m*-bromocinnamate. (*b*) Methyl *p*-bromocinnamate.

Table 8. *Methyl m-bromocinnamate*

Equations of best planes

		M_1	M_2	M_3	d
Benzene ring	C(5) · · · C(10)	6·8680	2·5987	−7·3409	1·5166
Ethylenic group	C(2) · · · C(5)	7·2933	1·6342	−8·2885	0·9935
	$C-CO_2$	7·3141	1·4294	−8·8199	0·7951

Equation of best plane: $M_1x+M_2y+M_3z-d=0$, where xyz are fractional coordinates.

Deviations from best planes (Å)

Atom	Benzene ring	Atom	Ethylenic group	Atom	$C-CO_2$
C(5)	−0·003	C(2)	−0·003	C(2)	−0·022
C(6)	−0·017	C(3)	0·003	C(3)	0·007
C(7)	0·017	C(4)	0·003	O(1)	0·007
C(8)	0·002	C(5)	−0·003	O(2)	0·010
C(9)	−0·021				
C(10)	0·022			C(1)	0·099

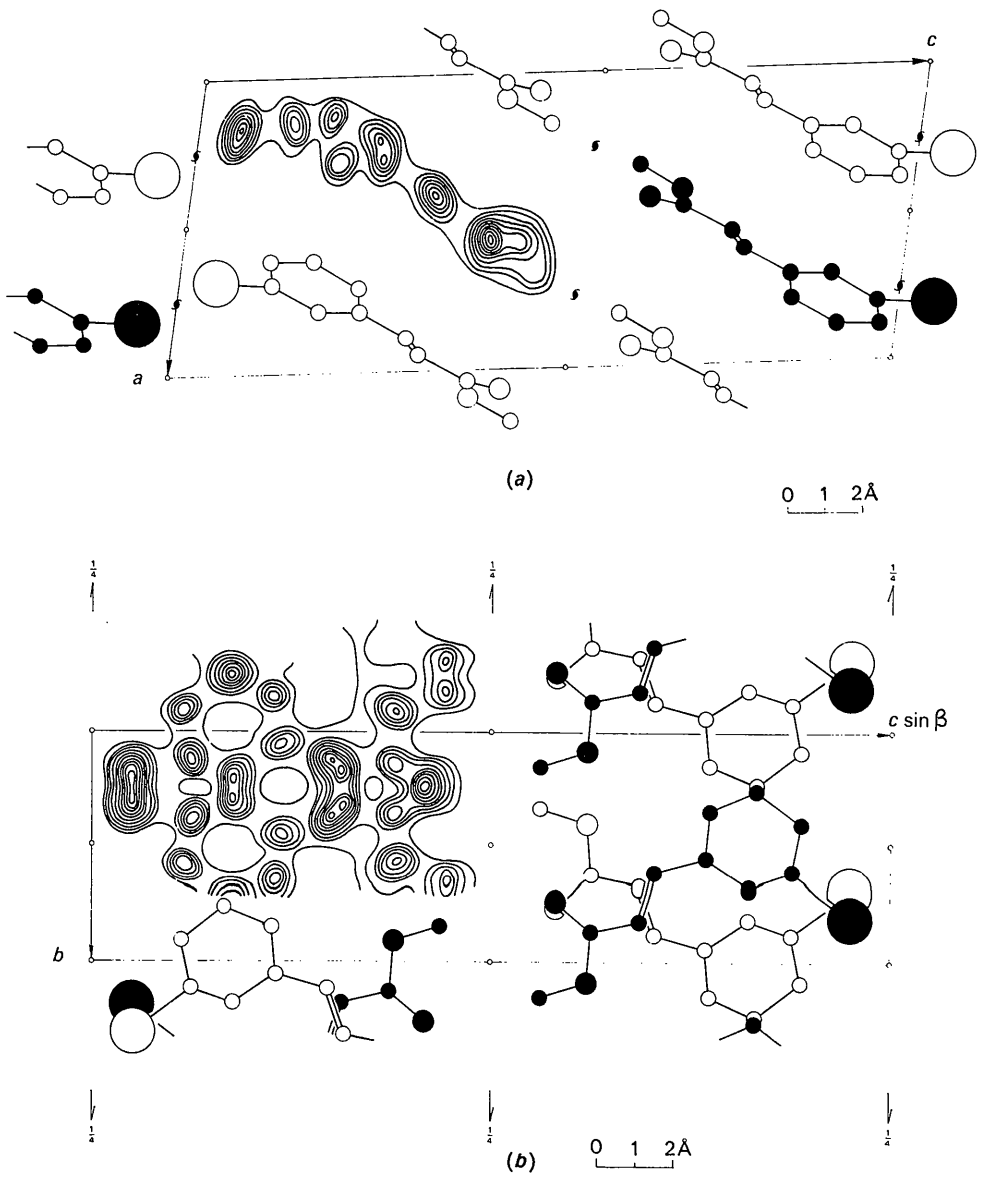


Fig. 3. Methyl *m*-bromocinnamate. Packing diagram and electron-density projection along (*a*) [010], (*b*) [100]. Contour interval 1 e.Å^{-2} except at bromine atom. Lowest contour 2 e.Å^{-2}.

Table 9. *Methyl p-bromocinnamate*

Equations of best planes

		M_1	M_2	M_3	d
Benzene ring	C(5) · · · C(10)	−4·5646	13·6065	−2·9218	3·6031
Ethylenic group	C(2) · · · C(5)	−3·7574	14·3926	−3·1637	3·9449
	C–CO_2	−4·1889	14·9627	−2·6772	4·5113

Equation of best plane: $M_1x+M_2y+M_3z-d=0$, where xyz are fractional coordinates.

Deviations from best planes (Å)

Atom	Benzene ring	Atom	Ethylenic group	Atom	C–CO_2
C(5)	−0·017	C(2)	−0·018	C(2)	0·004
C(6)	0·017	C(3)	0·015	C(3)	−0·002
C(7)	−0·004	C(4)	0·024	O(1)	−0·002
C(8)	−0·009	C(5)	−0·021	O(2)	−0·002
C(9)	0·008				
C(10)	0·005			C(1)	0·001

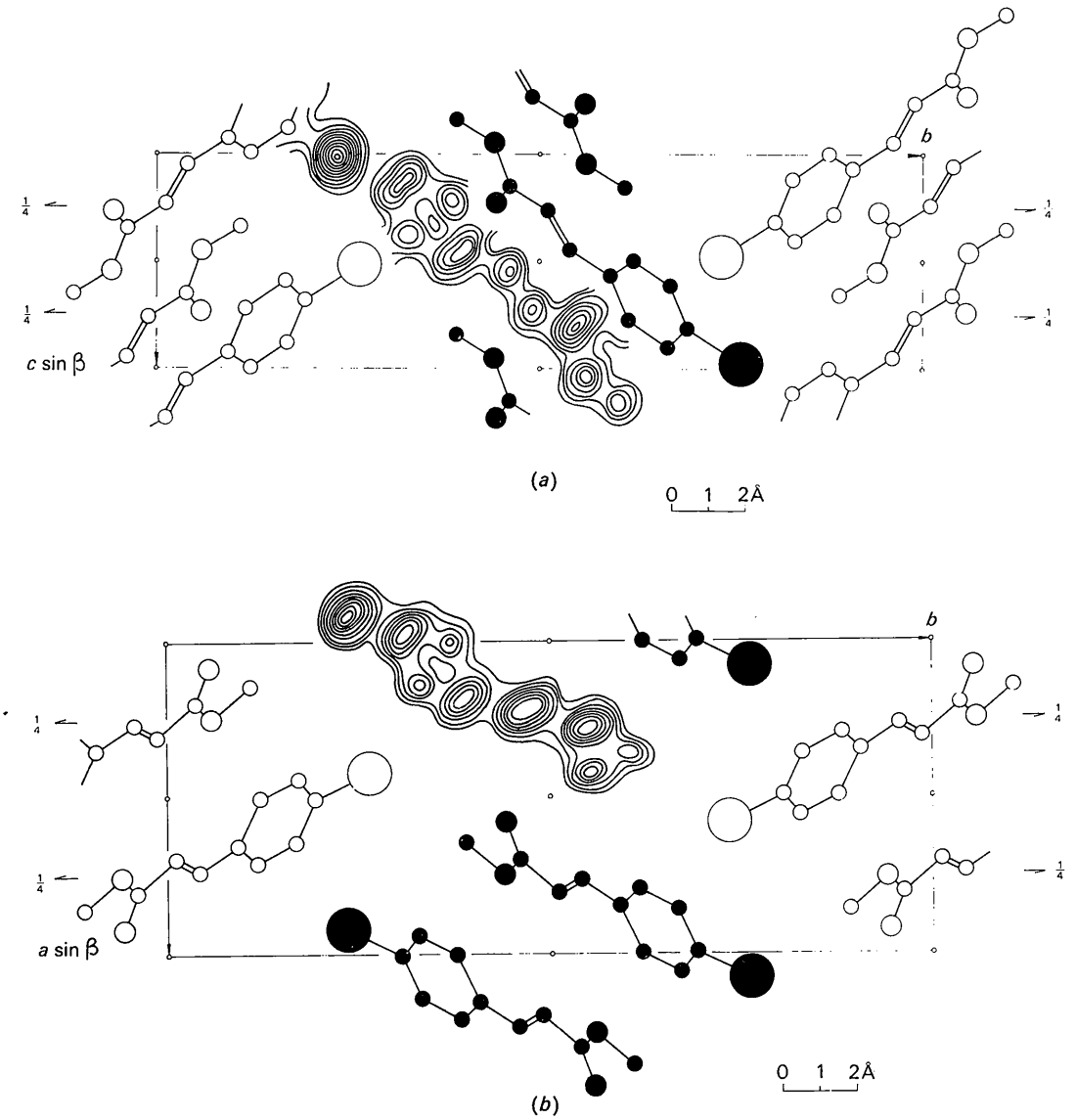


Fig. 4. Methyl *p*-bromocinnamate. Packing diagram and electron-density projection along (*a*) [100], (*b*) [001]. Contour intervals as in Fig. 3.

C_α–C_β and C=O bonds in the C_β–C_α–C(=O)–O system adopt the *cis* conformation around the C_α–C bond. Numerically, in the present instances, the two contacts C(4) · · · O(2) and H(4) · · · O(2) (calculated on the assumption of C–H = 1·08 Å and H(4)C(4)C(3) = 120°) are 2·86 and 2·55 Å, and 2·83 and 2·46 Å in the *m* and *p*-esters respectively. The corresponding C(4) · · · O(1) and H(4) · · · O(1) contact distances in the alternative *trans* conformation would be 2·58 and 2·16 Å, and 2·69 and 2·20 Å. Since the non-bonded contacts in the *cis* conformation are closer to the sums of the van der Waals radii of the atoms involved (C · · · O: 3·1 Å; O · · · H: 2·6 Å) the *cis* conformation is evidently preferred. The small angles of twist around the bond C(2)–C(3) (*m*: 2·5°; *p*: 5·2°) presumably permit conjugation between the >C=C< and the >C=O groups; in a hypothetical '*trans*' model, constructed with the observed non-bonded contact distances C(4) · · · O(2) and H(4) · · · O(2) the bond angles C(4)–C(3)–O(2) and C(3)–C(2)–O(1) would have to be increased or else the angle of twist between the >C=C< and the carboxylate groups increased by as much as 45°; the consequent loss of coplanarity would presumably lead to lowered conjugation as well as to less efficient packing.

The present argument can be extended to unsaturated as well as to saturated acids, and according to Table 10 is valid for all the acids listed there. The exception provided by α-*trans*-cinnamic acid, in which the >C=C< and >C=O groups lie in the *trans*-conformation, may well be due to the small difference between the C(3)–C(2)–O(1) and C(3)–C(2)–O(2) angles. In *o*-chloro- and *o*-bromobenzoic acids the significant non-bonded interactions are those between the halogen substituent on the '*β*' carbon and the oxygen atoms of the carboxyl group; according to Table 10 the observed *cis* conformation clearly provides for longer contacts and hence is sterically favoured.

In the amides such as succinamide (Davies & Pasternak, 1956) and *trans*-cinnamide (Osaki & Schmidt, unpublished) an additional interaction enters into the picture: the planar and near-planar configuration of all atoms including hydrogen in the system C–C–C(=O)–NH_2 would produce in the *trans* conformation of C_α–C_β and C=O too close an approach between a hydrogen atom of the NH_2 group and C_β and H_β (Table 10).

Table 10. *Non-bonded distances in cis and trans conformation of acids and amides*

Compound	C(3)–C(2)–O(1)	C(3)–C(2)–O(2)	C(4) · · · O(2)	C(4) · · · O(1)	Δ_1	H(4) · · · O(2)	H(4) · · · O(1)	Δ_2	Observed conformation	Reference
Valeric acid	117°	125°	2·88*	2·74†	0·14	2·78*	2·63†	0·15	*cis*	Scheuerman & Sass (1962)
β-Succinic acid	114°	124°	2·80*	2·60†	0·20	2·73*	2·53†	0·20	*cis*	Morrison & Robertson (1949*a*)
Sebacic acid	116°	120°	2·81*	2·77†	0·04	2·79*	2·73†	0·06	*cis*	Morrison & Robertson (1949*b*)
Acrylic acid	116°	122°	2·78*	2·67†	0·11	2·46*	2·33†	0·13	*cis*	Higgs & Sass (1963)
	113°	125°	2·86*	2·66†	0·20	2·57*	2·31†	0·26	*cis*	Chatani, Sakata & Nitta (1963)
Crotonic acid	113°	121°	2·83*	2·70†	0·13	2·56*	2·38†	0·18	*cis*	Robertson & Sutherland‡
Sorbic acid	116°	122°	2·85*	2·76†	0·09	2·60*	2·46†	0·14	*cis*	Robertson & Sutherland‡
α-*trans*-Cinnamic acid	115°	119°	2·77†	2·74*	0·03	2·44†	2·36*	0·08	*trans*	Ladell, McDonald & Schmidt
						Cl · · · O(2) 2·892*	Cl · · · O(1) 2·69†	0·20		
o-Chlorobenzoic acid	113°	122°								Ferguson & Sim (1961)
						Br · · · O(2) 3·004*	Br · · · O(1) 2·73*	0·27		
o-Bromobenzoic acid	114°	126°								Ferguson & Sim (1962)
	C(3)–C(2)–N	C(3)–C(2)–O(2)	C(4) · · · O(2)	C(4) · · · N	Δ_3	C(4) · · · H(N)	H(4) · · · H(N)			
Succinamide	116°	122°	2·80*	2·70†	0·10	2·22†	1·99†			Davies & Pasternak (1956)

Δ_1 = C(4) · · · O(2)–C(4) · · · C(1); Δ_2 = H(4) · · · O(2)–H(4) · · · O(1); Δ_3 = C(4) · · · O(2)–C(4) · · · N.
* Calculated from observed model. † Calculated for inverted model. ‡ Private communication.

Double-bond contacts

According to Fig. 3 the contact of nearest-neighbour >C=C< groups of the *m*-derivative is provided by the *a* glide, perpendicular to the short *b* axis; the molecular stack along *a* thus contains successive criss-crossed >C=C< bonds. This geometry of contact between the double bonds is therefore different from

that observed in the previously analysed cinnamic acid derivatives in which nearest-neighbour >C=C< groups are parallel (related by translation) or antiparallel (related by centres of symmetry). The centre-to-centre distance of nearest-neighbour >C=C< groups is 3·93 Å; contacts between C(3) and C(4′) and C(3′) and C(4) of adjacent glide-plane related molecules are 3·53 Å and 4·33 Å respectively. It follows from these values that interaction between two molecules is possible and likely to take place in the first instance between C(3) and C(4′).

The *p*-derivative displays the packing arrangement of the α type in the cinnamic acid series since contacts between nearest-neighbour >C=C< groups occur across centres of symmetry. Three sets of such contacts are present (Fig. 4); the centre-to-centre distances across the inversion centres at $(0\frac{1}{2}\frac{1}{2})$, $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, and $(0\frac{1}{2}0)$ are 4·11, 5·29, and 5·74 Å respectively. In the light of our previous results we should expect photochemical interaction across the centre at $(0\frac{1}{2}\frac{1}{2})$ with formation of the centrosymmetric dimer, dimethyl 4,4′-dibromo-α-truxillate.

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The Crystal and Molecular Structure of D(+)-Barium Uridine-5′-Phosphate*

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The crystal structure of hydrated barium uridine-5′-phosphate has been determined by three-dimensional Patterson and Fourier syntheses. The anomalous scattering of Cu *K* radiation by the barium (and phosphorus) atoms made it possible to confirm the absolute configuration of the molecule. The structure was refined by block diagonal least squares which made use of two unique octants of intensity data by incorporating the complex parts of the atomic scattering factors. The final *R* value was 9·8 % for 1502 $hk\bar{l}$ and 1000 hkl intensity data.

The geometry and absolute configuration of the molecule are in accord with previous studies on nucleotides. The barium ions lie in two independent special positions and each ion is surrounded by ten oxygen atoms. The nucleotides pack compactly, with pairs of base planes nearly parallel but only partially overlapping, and a close contact of O(1′) of one molecule with the pyrimidine ring of another. The conformation about the C(5′)-C(4′) bond in ribose derivatives and related molecules has been considered in detail, and its bearing on nucleotide conformation discussed. A suggested hydrogen-bonding scheme is illustrated.

Introduction

Divalent metal ions, especially those of the alkaline earths, play a significant part in the combination and the structural relationships of proteins and nucleic acids. The role of such ions in liberating DNA from nucleoproteins has been demonstrated by Kirby (1957, 1958). Dipositive cations are also known to act as catalysts in biological reactions of triphosphate nucleosides.

Various possibilities of coordination of dipositive cations with nucleotides have been discussed by Brint-

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