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Crystal and Molecular Structure of 5-(Bromomethylene)-10,11-dihydro-5H-dibenzo[a,d]-cycloheptene

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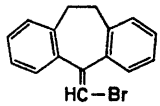
5-(Bromomethylene)-10,11-dihydro-5H-dibenzo[a,d]-cycloheptene has been studied in order to determine the molecular conformation of the pharmacologically active dibenzocycloheptene derivatives. The crystals are orthorhombic with $a=6.270$ Å, $b=9.288$ Å, $c=22.46$ Å. The unit cell contains four molecules, and the space group is $P2_12_12_1$. The seven-membered ring exists in a boat conformation, the long sides of which are formed by the bonds common with the benzene rings. The planes of the two benzene rings form a dihedral angle of 76°. A possible mechanism of action on the neuronal membrane is discussed.

Numerous tricyclic compounds are used as psychoactive agents. Certain dibenzoheptene derivatives are utilized in the therapy of depressions, whereas phenothiazines of various kinds are used as tranquillizers. The molecules of these two types of tricyclic compounds, which are relatively similar, can thus exhibit opposite pharmacological effects. This has been a reason for extensive speculations on their molecular geometry.

A crystal structure study was undertaken by the present author in order to provide information on the detailed molecular conformation in these active tricyclic compounds. As will be discussed below it is believed that drugs of this type act on the biological membranes, and knowledge on the structure of the drug as well as of the membrane is needed in order to understand their function on a molecular level.

The structural formula of 5-(bromomethylene)-10,11-dihydro-5H-dibenzo [a,d]cycloheptene is:



If the bromine atom is replaced by a $-CH_2-CH_2-N(CH_3)_2$ group a wellknown antidepressive agent called amitriptylin is obtained.

PREPARATION OF CRYSTALS

5-(Bromomethylene)-10,11-dihydro-5H-dibenzo[a,d]-cycloheptene was prepared according to a method described by Ebnöther *et al.*,[1] and crystals for X-ray work were grown from ethanol at room temperature. The crystals form needles parallel to the *a*-axis with a cross-section of hexagonal appearance (edges parallel to the *b*-axis and two *bc*-diagonals).

X-RAY DATA

Rotation and Weissenberg photographs were taken about the *a*- and *b*-axis with a calibrated camera using Cu$K\alpha$ radiation. The following X-ray data were obtained:

Unit cell: orthorhombic
$a = 6.270 \pm 0.009$ Å, $b = 9.288 \pm 0.012$ Å, $c = 22.46 \pm 0.03$ Å.
Space group: $P2_12_12_1$.
Four molecules per unit cell.
Density calculated: 1.45 g.cm^{-3}.
Density measured: 1.43 g.cm^{-3}.

The reflection intensities were measured using an on-line automatic scanner developed by Abrahamsson.[2] The corresponding operation programs produce a paper tape with indices and integrated intensity values of the spots on the films which can be used directly as input to the data reduction program. The film factors were plotted against the intensity values for each film pack, and from this plot the most reliable intensity interval was estimated. The final intensity values were then selected from these intervals.

The reflection intensities were corrected for the Lorentz and polarization factors but not for absorption. Absolute values were later obtained by comparison with calculated structure factors.

STRUCTURE DETERMINATION

The position of the bromine atom in the asymmetric unit was derived from the Patterson function, which was sharpened to correspond to point atoms at rest. The carbon atoms were then located by successive cycles of structure factors calculations and Fourier syntheses.

The structure was refined by block-diagonal and full matrix least-squares treatment using anisotropic temperature factors. When an R value of 0.20 was reached a difference synthesis was calculated. All hydrogen atoms could then be located. The hydrogen atoms were included in the following least-squares refinement with calculated positions, as the corresponding peaks in the Fourier maps were too broad to give positions of reasonable accuracy. The hydrogen positions were not refined but recalculated after each round of least-squares refinement. Isotropic temperature factors were used for the hydrogen atoms calculated from the mean-square amplitude tensor of the corresponding hydrogen-carrying atom. When all shifts were less then one-third of the standard deviations the refinement was stopped. The final R value for the 611 observed reflections was 0.12.

The scattering curves given in the *International Tables for X-ray Crystallography*, Vol. III (1962), were used. The calculations were performed on the Datasaab D21 computer using a program system developed at this Institute.[3] The weighting scheme applied in the refinement was:

$$w = \frac{1}{1 + [(|F_o| - 8|F_{min}|)/5|F_{min}|]^2}$$

RESULTS AND DISCUSSION

Observed and calculated structure factors are listed in Table 1. Final atomic positions are given in Table 2. The vibration tensor elements for non-hydrogen atoms are given in Table 3. Isotropic temperature factors were used for hydrogen atoms averaged from the mean-square amplitude tensors of the corresponding hydrogen-carrying atom.

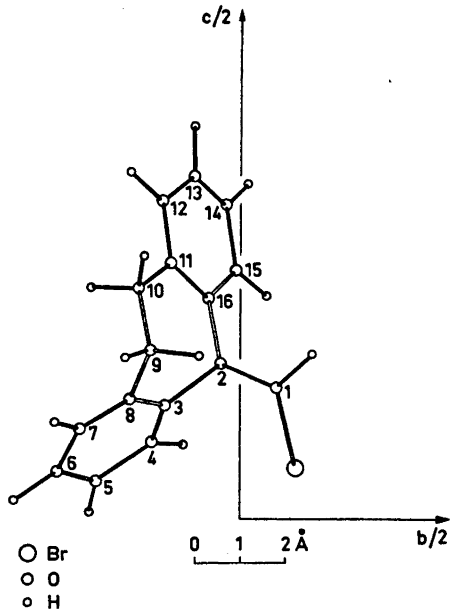


Fig. 1. Stereochemistry of 5-(bromomethylene)-10,11-dihydro-5H-dibenzo[a,d]-cycloheptene.

The stereochemistry of the molecule is shown in Fig. 1. The seven-membered ring exists in a boat form although irregular as will be described below, and the long sides are formed by the bonds which are common with the benzene rings. Bond distances and angles are given in Tables 4 and 5. The sp^3-carbon atoms in the seven-membered ring have an average bond angle of 114.5°. Enlarged angles in seven-membered rings have been discussed by Asher and Sim.[4] The planes of the two benzene rings and adjacent bonds form a dihedral angle of 76°. The geometry of the seven-membered ring is

Table 1. Observed and calculating structure factors (×100) and phase angles as fraction of one revolution.

h	k	l	Fobs	Fcalc	Fi	h	k	l	Fobs	Fcalc	Fi	h	k	l	Fobs	Fcalc	Fi
0	0	4	1834	1883	1.0000	0	6	6	2240	2110	0.5000	1	4	2	5254	4509	0.0332
0	0	6	5680	5916	0.5000	0	6	7	5023	4791	1.0000	1	4	3	2149	1783	0.6874
0	0	8	7411	7668	0.5000	0	6	8	2362	2153	0.5000	1	4	4	7398	8293	0.9823
0	0	10	10073	10658	0.5000	0	6	10	2265	2266	0.5000	1	4	5	4466	3509	0.0626
0	0	12	5372	5301	0.5000	0	6	11	2350	2365	0.5000	1	4	6	6882	7841	0.9936
0	0	14	3747	3868	0.5000	0	6	13	3394	3479	0.5000	1	4	7	3299	3127	0.6257
0	0	16	2798	1964	1.0000	0	6	14	2486	2360	0.5000	1	4	8	3817	4192	0.9979
0	0	18	4370	3899	1.0000	0	6	15	3062	3298	0.5000	1	4	9	3308	3092	0.5896
0	0	20	4262	3516	1.0000	0	6	20	2161	2489	1.0000	1	4	12	3706	3670	0.5020
0	1	1	868	467	0.2502	0	7	1	2381	2652	0.7500	1	4	14	4955	5197	0.4554
0	1	2	5229	4873	0.2500	0	7	2	1987	1901	0.2500	1	4	16	4203	4395	0.5064
0	1	3	5971	5218	0.2500	0	7	3	1744	1633	0.7500	1	4	17	2614	2513	0.2486
0	1	4	5368	5295	0.2500	0	7	4	6198	6261	0.2500	1	4	18	2625	2565	0.5321
0	1	5	4013	3659	0.2500	0	7	6	4337	5096	0.2500	1	4	19	1860	1571	0.8588
0	1	6	2076	2379	0.2500	0	7	7	1720	958	0.7500	1	5	0	4103	3669	0.7500
0	1	7	2041	2120	0.7500	0	7	8	3183	2870	0.2500	1	5	1	2417	2068	0.3138
0	1	8	2535	2528	0.2500	0	7	9	2031	2125	0.2500	1	5	2	2680	2385	0.6827
0	1	9	8265	9094	0.7500	0	7	11	2489	2335	0.2500	1	5	3	6439	6318	0.2522
0	1	10	3397	2901	0.2500	0	7	12	2170	2411	0.7500	1	5	4	2119	1404	0.8762
0	1	11	3551	4230	0.7500	0	7	14	4028	4179	0.7500	1	5	5	6600	6362	0.2666
0	1	12	6556	6370	0.7500	0	7	16	3644	3696	0.7500	1	5	7	6042	5815	0.2374
0	1	13	3978	4539	0.7500	0	8	0	3988	3613	1.0000	1	5	8	1787	1483	0.2452
0	1	14	3660	3424	0.7500	0	8	2	3469	3672	1.0000	1	5	9	1937	1521	0.1936
0	1	15	2349	2181	0.2500	0	8	3	2259	2370	0.5000	1	5	10	3683	3636	0.2992
0	1	16	3144	3730	0.7500	0	8	4	1955	1794	1.0000	1	5	11	2609	2652	0.7830
0	1	17	2351	2630	0.2500	0	8	5	3184	3099	0.5000	1	5	12	2618	2934	0.2725
0	1	18	1409	1496	0.7500	0	8	6	1987	1821	0.5000	1	5	13	5915	5501	0.7614
0	1	19	2981	2440	0.2500	0	8	7	2878	3318	0.5000	1	5	15	2809	2454	0.7526
0	1	20	1571	1324	0.2500	0	8	8	2552	2962	0.5000	1	5	17	3705	3480	0.7878
0	1	21	4088	4577	0.2500	0	9	1	3466	3956	0.2500	1	6	1	7409	6924	0.0897
0	2	0	4731	3949	0.5000	0	10	2	2010	2271	0.5000	1	6	3	3540	3317	0.0498
0	2	1	3570	2534	1.0000	0	10	8	2052	1868	1.0000	1	6	4	3771	3254	0.9436
0	2	2	3369	2194	0.5000	1	0	2	12366	13490	0.5000	1	6	7	3555	3343	0.5255
0	2	3	15104	15634	0.5000	1	0	3	1569	1043	0.7499	1	6	9	5453	4998	0.4906
0	2	4	3007	2199	1.0000	1	0	4	15971	16631	0.5000	1	6	11	5195	4850	0.4674
0	2	5	13823	13852	0.5000	1	0	5	3283	3319	0.2500	1	6	16	1979	2007	0.9621
0	2	6	3201	2197	1.0000	1	0	6	8431	8849	0.5000	1	6	19	3047	3161	0.9864
0	2	7	8634	8297	0.5000	1	0	8	3622	4465	0.5000	1	6	21	1707	1895	0.9050
0	2	8	1118	1383	1.0000	1	0	10	4597	4497	0.5000	1	7	0	5633	5098	0.2500
0	2	9	3451	3692	0.5000	1	0	12	6389	5757	1.0000	1	7	1	2649	1911	0.2567
0	2	11	1519	990	1.0000	1	0	14	5810	6709	1.0000	1	7	2	5478	4842	0.2070
0	2	13	7373	7189	1.0000	1	0	16	3788	4762	1.0000	1	7	4	2968	2407	0.1909
0	2	15	5572	5389	1.0000	1	1	0	12122	13141	0.2500	1	7	6	2417	1972	0.7480
0	2	16	1714	1332	0.5000	1	1	1	2511	2102	0.1917	1	7	8	4733	4282	0.7798
0	2	17	4188	3972	1.0000	1	1	2	3277	4318	0.4532	1	7	9	1645	1959	0.2759
0	2	18	2136	1704	0.5000	1	1	3	4603	6282	0.8237	1	7	10	5039	5056	0.7598
0	2	19	2205	1934	1.0000	1	1	4	3213	3092	0.9499	1	7	12	2645	2400	0.7646
0	2	20	1310	1112	1.0000	1	1	5	5682	6579	0.6760	1	7	14	2110	2095	0.7945
0	2	25	3529	3212	0.5000	1	1	6	2842	1883	0.7764	1	7	15	2124	1859	0.7067
0	3	1	7595	7138	0.2500	1	1	7	6029	7161	0.6797	1	7	16	1840	2088	0.3004
0	3	2	6077	5796	0.7500	1	1	8	2674	2978	0.7952	1	7	18	2319	2621	0.2681
0	3	3	1216	213	0.7497	1	1	9	3190	2607	0.7905	1	8	1	1861	1908	0.4916
0	3	4	9731	9216	0.7500	1	1	10	4811	5749	0.7247	1	8	3	2517	2562	0.5355
0	3	5	2154	1531	0.7500	1	1	11	3984	3617	0.2963	1	8	4	4057	3874	0.5053
0	3	6	6503	5672	0.7500	1	1	12	3940	3866	0.7644	1	8	6	4291	4217	0.5258
0	3	8	2743	2860	0.7500	1	1	13	5505	5398	0.1987	1	8	7	2830	3074	0.0996
0	3	9	3273	3451	0.7500	1	1	15	3330	3338	0.2800	1	8	8	1997	2346	0.5163
0	3	10	1644	972	0.2500	1	1	16	2469	1869	0.1287	1	8	9	2048	2337	0.0443
0	3	11	4348	4057	0.7500	1	1	17	3165	3219	0.2388	1	8	14	2539	2920	0.0033
0	3	12	3664	3507	0.2500	1	1	18	3149	2862	0.2259	1	8	16	2002	2209	0.9778
0	3	13	2462	2987	0.7500	1	1	20	2806	2646	0.2714	1	9	1	2338	1622	0.8208
0	3	14	5671	5393	0.2500	1	1	23	2826	2693	0.7910	1	9	2	2480	2111	0.3232
0	3	16	3787	4034	0.2500	1	1	25	2240	2999	0.7286	1	9	3	2903	3293	0.7827
0	3	17	3330	3490	0.2500	1	2	0	1967	1938	0.7500	1	9	4	1545	1321	0.2735
0	3	18	1992	1408	0.2500	1	2	1	15171	15180	0.4199	1	9	5	4697	4798	0.7374
0	3	19	1433	1180	0.2500	1	2	2	1778	1925	0.3784	1	9	7	3088	3137	0.7232
0	4	0	9138	8731	0.5000	1	2	3	8981	8820	0.6223	1	9	15	2018	2522	0.2681
0	4	1	1575	909	0.5000	1	2	4	6001	6749	0.0890	1	10	1	1931	2692	0.4734
0	4	2	10902	10032	0.5000	1	2	5	2135	1162	0.5945	1	10	6	1598	2324	0.0315
0	4	4	2569	2300	0.5000	1	2	6	2507	1944	0.5479	2	0	3	2537	1608	0.2500
0	4	5	1419	1306	1.0000	1	2	7	4623	4807	0.9416	2	0	4	1524	376	0.9999
0	4	6	2965	2390	1.0000	1	2	8	2800	1904	0.4150	2	0	5	3504	3435	0.2500
0	4	7	3572	3636	1.0000	1	2	9	10583	10643	0.2872	2	0	6	1158	1886	0.5000
0	4	8	7050	7131	1.0000	1	2	10	2454	2857	0.7365	2	0	7	2112	2634	0.7500
0	4	10	7245	6888	1.0000	1	2	11	6511	6877	0.0056	2	0	8	5725	5699	1.0000
0	4	11	997	898	0.5000	1	2	12	2263	1664	0.7609	2	0	9	2456	2493	0.7500
0	4	12	4083	5089	1.0000	1	2	13	5459	5055	0.0280	2	0	10	7353	7641	1.0000
0	4	13	2526	3052	0.5000	1	2	14	2688	1939	0.6186	2	0	11	1516	1619	0.7500
0	4	14	2173	2049	1.0000	1	2	17	3636	3283	0.5171	2	0	12	7800	7233	1.0000
0	4	17	2303	2295	0.5000	1	2	19	3134	2307	0.4734	2	0	14	1629	1707	1.0000
0	4	18	3136	3014	0.5000	1	2	21	4525	4059	0.4887	2	0	18	3704	3596	0.5000
0	4	20	4004	3410	0.5000	1	3	0	10738	11141	0.7500	2	0	20	3530	3788	0.5000
0	5	1	8254	7926	0.7500	1	3	1	1491	982	0.4888	2	1	0	2106	1236	1.0000
0	5	2	1114	782	0.7499	1	3	2	5186	5531	0.7173	2	1	1	9268	8865	0.7180
0	5	3	1790	2129	0.7500	1	3	3	5499	6514	0.7547	2	1	2	8732	8332	0.7221
0	5	5	1074	556	0.7499	1	3	4	3799	3242	0.6351	2	1	3	3351	3668	0.6711
0	5	6	4264	4582	0.7500	1	3	5	4533	4417	0.8018	2	1	4	3226	3646	0.7383
0	5	7	4774	4296	0.2500	1	3	6	4187	4079	0.3021	2	1	5	2066	1335	0.4982
0	5	8	2231	2209	0.7500	1	3	7	3176	2593	0.8931	2	1	6	4041	4172	0.8194
0	5	9	6520	6495	0.2500	1	3	8	5323	5918	0.2708	2	1	7	6551	6063	0.2905
0	5	10	2881	2521	0.7500	1	3	9	1411	994	0.7813	2	1	8	3440	2263	0.6918
0	5	11	5854	5770	0.2500	1	3	10	5423	5789	0.1593	2	1	9	5446	4931	0.2422
0	5	14	4097	4172	0.2500	1	3	11	1966	1066	0.5581	2	1	10	1566	1088	0.0052
0	5	16	1319	287	0.2500	1	3	12	4382	3960	0.2464	2	1	11	5364	4836	0.1965
0	5	17	2713	2847	0.7500	1	3	13	3407	2900	0.2443	2	1	12	3000	3182	0.1779
0	5	19	3795	3802	0.7500	1	3	14	2447	2461	0.2445	2	1	13	1568	1945	0.1598
0	6	0	2406	1998	1.0000	1	3	15	5322	4940	0.2937	2	1	14	3965	4065	0.2035
0	6	1	4466	4472	1.0000	1	3	16	3793	3750	0.7062	2	1	16	2334	2482	0.3857
0	6	2	1635	1691	1.0000	1	3	18	3536	2964	0.7699	2	1	17	1999	2811	0.8555
0	6	3	6247	6023	1.0000	1	3	20	3392	3345	0.8004	2	1	18	2056	2439	0.2479
0	6	4	3209	2921	1.0000	1	4	0	5777	5561	0.7500	2	2	0	974	564	0.9999
0	6	5	6768	6307	1.0000	1	4	1	1980	1397	0.9584	2	2	1	2368	2318	0.8311

Table 1. Continued.

h	k	l	Fobs	Fcalc	Fi
2	2	2	2198	1356	0.4667
2	2	3	6948	7257	0.9915
2	2	4	2460	2150	0.8654
2	2	5	6556	7563	0.0028
2	2	6	2132	2365	0.6761
2	2	7	7011	7197	0.0008
2	2	8	4276	3760	0.6886
2	2	9	4649	4453	0.0959
2	2	10	1784	871	0.8101
2	2	11	3302	2662	0.5111
2	2	13	5702	5144	0.5310
2	2	14	2418	2314	0.1054
2	2	15	5916	5809	0.4813
2	2	16	2644	2561	0.0428
2	2	17	2112	2323	0.5174
2	3	1	3482	3592	0.8093
2	3	2	4781	4684	0.3174
2	3	3	5660	5235	0.8301
2	3	4	8629	9100	0.2747
2	3	5	4121	2906	0.2796
2	3	6	5725	5209	0.2064
2	3	8	3551	3724	0.1176
2	3	9	4120	3834	0.3206
2	3	10	2019	1735	0.0916
2	3	11	1564	2250	0.2750
2	3	12	3137	3253	0.7347
2	3	13	2762	2219	0.3203
2	3	14	4184	3373	0.7280
2	3	16	4474	4997	0.7444
2	4	0	9304	9769	1.0000
2	4	2	3863	3194	0.9778
2	4	3	1999	2355	0.6723
2	4	4	4271	3573	0.0422
2	4	5	1686	1472	0.4797
2	4	6	4446	3919	0.4174
2	4	7	1372	961	0.5533
2	4	8	4155	3273	0.5133
2	4	9	1404	596	0.1601
2	4	10	6892	5950	0.4585
2	4	11	3452	3658	0.1134
2	4	12	5356	5013	0.5071
2	4	13	3005	2706	0.1415
2	4	14	1641	2208	0.6265
2	4	15	1674	1783	0.4884
2	4	16	1949	2492	0.9703
2	4	18	1989	2777	0.9592
2	4	20	1885	2618	0.0214
2	5	0	1177	1633	1.0000
2	5	1	6577	6428	0.2367
2	5	2	3371	2883	0.2655
2	5	3	3228	3336	0.2482
2	5	4	2525	2414	0.1591
2	5	5	1964	1675	0.1687
2	5	6	2950	3019	0.3151
2	5	7	4616	4156	0.8162
2	5	9	7330	6828	0.7746
2	5	11	4018	4029	0.7258
2	5	12	1914	1975	0.8002
2	5	13	1671	1740	0.7204
2	6	0	1948	1935	0.5000
2	6	1	1619	2330	0.3758
2	6	2	2893	2937	0.3725
2	6	3	4824	4386	0.4743
2	6	5	4016	3763	0.5360
2	6	7	3781	4206	0.5020
2	6	9	1463	1558	0.5383
2	6	13	2789	3737	0.9342
2	6	15	2301	3030	0.9792
2	7	1	3134	3334	0.1939
2	7	2	2688	2992	0.8374
2	7	4	5141	5483	0.7493
2	7	6	4828	5045	0.7426
2	8	2	3277	4010	0.5713
2	9	1	3401	3996	0.7078
3	0	2	4186	4988	1.0000
3	0	3	3605	3061	0.7500
3	0	4	3964	3709	1.0000
3	0	5	2604	2370	0.7500
3	0	6	5077	4441	1.0000
3	0	8	6121	5483	1.0000
3	0	9	1406	702	0.2500
3	0	10	2130	1442	1.0000
3	0	11	1652	1541	0.7500
3	0	12	4641	4185	0.5000
3	0	13	2382	1851	1.0000
3	0	14	2393	2823	0.5000
3	0	15	2502	2680	0.7500
3	0	16	4233	4416	0.5000
3	0	17	2599	2971	0.2500
3	0	18	2645	2681	0.5000
3	1	0	7491	6915	0.7500
3	1	1	2900	2131	0.3901
3	1	2	3495	3054	0.7360
3	1	3	6498	6957	0.2700
3	1	4	2512	1962	0.0187
3	1	5	4885	5802	0.2955
3	1	6	1871	1687	0.1276
3	1	7	3236	3461	0.1565
3	1	8	5452	4470	0.1363
3	1	9	2072	2441	0.0989
3	1	10	3303	2912	0.2984
3	1	11	2458	2927	0.8430
3	1	12	3673	3531	0.2926
3	1	13	3924	3604	0.8169
3	1	15	2757	2438	0.7278
3	2	0	2597	2992	0.7500
3	2	1	4307	5225	0.0754
3	2	2	2467	1921	0.8633
3	2	3	5041	4786	0.9775
3	2	4	1897	1516	0.7763
3	2	5	2677	2344	0.2091
3	2	6	1696	1488	0.4401
3	2	7	4310	3712	0.5431
3	2	9	4812	4808	0.4950
3	2	10	1662	1854	0.2290
3	2	11	4524	4657	0.4763
3	2	13	3311	3075	0.5416
3	2	14	2123	1448	0.3040
3	2	15	2140	2194	0.9271
3	2	16	2185	1787	0.9802
3	2	17	2124	1785	0.0820
3	2	18	2007	1291	0.2845
3	3	0	7351	7142	0.2500
3	3	1	2069	2023	0.1379
3	3	2	4801	4604	0.2348
3	3	3	2348	2432	0.1486
3	3	4	2006	2532	0.1048
3	3	5	1974	2944	0.2952
3	3	6	2185	2834	0.8463
3	3	7	2532	2381	0.2515
3	3	8	3432	3436	0.8064
3	3	9	1637	1501	0.4111
3	3	10	3693	3717	0.7667
3	3	11	1716	2338	0.6180
3	3	12	3321	3907	0.6915
3	3	14	3347	2615	0.6920
3	3	15	2060	2320	0.6849
3	3	16	2254	2021	0.3779
3	3	17	2213	2072	0.8907
3	3	18	2109	2355	0.3117
3	3	20	1825	2253	0.2916
3	4	0	2119	1170	0.2500
3	4	1	1792	1743	0.2997
3	4	2	5366	4233	0.4928
3	4	3	1563	1095	0.2838
3	4	4	5841	4558	0.4756
3	4	5	1642	1898	0.2538
3	4	6	3664	3679	0.5163
3	4	7	2200	2577	0.1416
3	4	8	2129	2463	0.5293
3	4	9	2267	2625	0.0492
3	4	10	2120	1369	0.7055
3	4	12	2129	2401	0.9624
3	4	13	2172	1683	0.5099
3	4	14	3605	4218	0.9837
3	4	15	1720	2047	0.5465
3	4	16	2220	2662	0.9997
3	5	0	1631	1628	0.2500
3	5	1	1897	1957	0.8036
3	5	2	2168	2610	0.3354
3	5	3	3878	3158	0.7846
3	5	4	2148	1265	0.3078
3	5	5	5929	5264	0.7899
3	5	6	2365	2583	0.6259
3	5	7	5743	5158	0.7424
3	5	8	1600	1513	0.7877
3	5	9	2017	1726	0.6198
3	5	10	2006	2546	0.6851
3	5	11	2281	2708	0.3738
3	5	12	1465	1210	0.8045
3	5	13	2265	2258	0.2224
3	5	17	2523	3079	0.2762
3	6	0	1374	1668	0.2500
3	6	1	5454	4174	0.4285
3	6	3	2336	2587	0.6515
3	6	4	2579	2564	0.0168
3	6	5	989	411	0.0059
3	6	6	1662	1475	0.7464
3	6	7	1979	1869	0.8248
3	6	8	1863	1078	0.6491
3	6	9	2296	2805	0.0316
3	6	11	2870	3710	0.9681
3	6	13	1947	1608	0.0961
3	7	0	2461	2948	0.7500
3	7	1	1949	1900	0.7068
3	7	2	3606	4214	0.7593
3	7	3	2205	2495	0.6824
3	7	4	1808	1962	0.7422
3	7	6	1924	2152	0.3484
3	7	8	2894	3754	0.2997
3	7	10	2411	3304	0.2307
3	7	12	1843	1995	0.2870
3	8	4	1937	2476	0.9856
3	8	6	2574	3775	0.0191
3	8	8	1614	1515	0.9381
4	0	2	1118	1408	1.0000
4	0	3	2807	837	0.7500
4	0	4	2301	2237	1.0000
4	0	5	1204	1224	0.2500
4	0	6	2055	2381	0.5000
4	0	7	911	620	0.7500
4	0	8	1832	2180	0.5000
4	0	9	2448	1859	0.2500
4	0	10	2470	2566	0.5000
4	0	12	4198	3854	0.5000
4	1	0	2404	2084	1.0000
4	1	1	3113	3350	0.2520
4	1	2	3415	2468	0.2082
4	1	3	2977	2454	0.1877
4	1	4	4258	3711	0.1445
4	1	7	3451	3172	0.9207
4	1	8	3884	2943	0.3641
4	1	9	4875	4320	0.7518
4	1	10	2650	3259	0.4821
4	1	11	2198	1962	0.7971
4	1	12	2594	3028	0.7278
4	1	13	3224	2794	0.5954
4	2	0	1589	1397	1.0000
4	2	1	1415	1616	0.4162
4	2	2	1352	1490	0.3952
4	2	3	3739	3301	0.5170
4	2	4	2191	2249	0.2226
4	2	5	4541	4230	0.5332
4	2	6	1796	1974	0.1944
4	2	7	3359	3009	0.4678
4	2	9	1935	1298	0.5087
4	2	10	825	1161	0.5186
4	2	11	2269	2314	0.9927
4	2	13	3282	2991	0.8927
4	3	0	1314	604	1.0000
4	3	1	2470	1627	0.2297
4	3	2	2842	3080	0.8527
4	3	3	1814	1972	0.3741
4	3	4	4176	3610	0.7338
4	3	5	1032	1546	0.4794
4	3	6	2508	2872	0.7688
4	3	7	2219	2559	0.6560
4	3	8	2152	1725	0.7165
4	3	9	1190	1537	0.5625
4	3	10	1737	2263	0.5686
4	3	11	1786	2621	0.7507
4	3	12	1582	1651	0.4516
4	3	13	1314	1616	0.9065
4	3	14	2815	3257	0.3295
4	3	16	2636	2513	0.2265
4	4	0	1879	2181	0.5000
4	4	1	1333	2142	0.1921
4	4	2	4390	4708	0.5251
4	4	4	1710	2383	0.8210
4	4	8	1956	3009	0.0115
4	4	11	2069	3068	0.5699
4	4	12	2291	2608	0.0708
4	5	0	1489	2354	0.5000
4	5	1	3105	3247	0.7037
4	5	2	1498	1455	0.6349
4	5	3	1510	2202	0.7432
4	5	9	2465	2760	0.3196
4	5	11	2488	3037	0.2021
5	0	2	3697	3550	0.5000
5	0	3	523	106	0.2502
5	0	4	2452	2910	0.5000
5	0	5	2024	1640	0.2500
5	1	0	1660	1890	0.2500
5	1	1	1953	1603	0.9073
5	1	2	1512	1365	0.3025
5	1	3	1965	1190	0.0557
5	1	4	2807	1789	0.4932
5	1	5	2843	3212	0.7627
5	1	6	1952	2817	0.5195
5	1	7	2083	1699	0.6900
5	1	9	1694	2061	0.5851
5	1	10	1762	2715	0.7049
5	1	11	2279	2418	0.3812
5	1	12	1571	1504	0.9032
5	2	1	3643	3009	0.4122
5	2	2	845	1510	0.2186
5	2	3	2877	2850	0.6378
5	2	4	1924	1812	0.0011
5	2	5	2098	1624	0.2230
5	2	6	1442	1624	0.5100
5	2	7	1948	2049	0.9582
5	2	8	641	1135	0.8328
5	2	9	1627	2040	0.9685
5	2	11	1714	1977	0.9617
5	3	1	812	1681	0.5317
5	3	2	2604	2250	0.7118
5	3	3	1571	1978	0.7291
5	3	4	1054	1323	0.4798
5	3	5	1398	1239	0.5598
5	3	6	910	646	0.5773
5	3	8	2248	2590	0.3512
5	3	9	1199	1736	0.0014
5	3	12	2770	2653	0.2678
5	3	13	1746	2044	0.1622
5	3	14	1862	1410	0.0434
5	4	0	1593	1201	0.7500
5	4	1	1304	861	0.1712
5	4	2	1735	954	0.9615
5	4	3	662	1579	0.7473
5	4	4	2012	2224	0.0231
5	4	5	1798	1462	0.8125
5	4	6	1824	2485	0.0404
5	4	8	706	829	0.0536
5	4	9	1425	1285	0.4678

quite unsymmetrical compared to those found in other compounds (*cf.* Ref. 5). This is a consequence of the steric requirements due to the bond situation in the ring. The carbon atom C2 is situated within 0.02 Å in the intersection of the planes of the two benzene rings, whereas the carbon atoms C9 and C10 are situated in the planes of the benzene rings C3–C8 and C11–C16, respectively, (distances 0.01 Å and 0.04 Å). The carbon atom C9 is located 0.95 Å from the best least-squares plane through the four carbon atoms of the seven-membered ring which are common to the benzene rings, and the corresponding distance for C10 is 0.19 Å.

Table 2. Fractional coordinates for the atoms of one molecule. The numbering for non-hydrogen atoms is shown in Fig. 1. The hydrogen atoms are numbered in the same way as their parent atom with the addition of one last digit to indicate the number attached to the same parent atom.

	x	*y*	*z*
Br	0.2312	1.1352	0.0505
C(1)	0.2753	1.0849	0.1284
C(2)	0.2529	0.9502	0.1515
C(3)	0.2454	0.8176	0.1113
C(4)	0.0939	0.7873	0.0754
C(5)	0.0995	0.6593	0.0363
C(6)	0.2998	0.5666	0.0442
C(7)	0.4602	0.6159	0.0862
C(8)	0.4312	0.7422	0.1178
C(9)	0.6183	0.7849	0.1653
C(10)	0.5312	0.7556	0.2254
C(11)	0.3426	0.8351	0.2501
C(12)	0.2599	0.8151	0.3108
C(13)	0.0993	0.8915	0.3338
C(14)	−0.0228	0.9701	0.3040
C(15)	0.0144	0.9932	0.2444
C(16)	0.1889	0.9248	0.2169
H(11)	0.326	1.169	0.158
H(41)	−0.043	0.860	0.073
H(51)	−0.026	0.638	0.004
H(61)	0.324	0.465	0.021
H(71)	0.605	0.553	0.092
H(91)	0.758	0.721	0.157
H(92)	0.654	0.899	0.161
H(101)	0.484	0.640	0.225
H(102)	0.661	0.769	0.256
H(121)	0.337	0.733	0.338
H(131)	0.071	0.884	0.381
H(141)	−0.156	1.021	0.325
H(151)	−0.090	1.061	0.218

The C–Br bond seems to be significantly shorter than olefinic carbon-bromine distances in general (1.89±0.01 Å according to *The International Tables for X-Ray Crystallography*, Vol. III (1962) p. 273). This might be an inductive effect due to the vicinity of the π-electron orbitals of the conjugated systems of the molecule.

Table 3. Vibration parameters. Anitsotropic temperature factors were used in the refinement according to $\exp[-2^2(h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2klbcU_{23} + 2hlacU_{13} + 2hkabU_{12})]$. The tensor elements in Å² have been multiplied by 1000.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{31}	U_{12}
Br	712	257	417	109	81	17
C(1)	1108	156	401	95	−1064	13
C(2)	820	342	233	−69	−304	663
C(3)	641	227	−68	38	279	21
C(4)	725	491	19	206	−23	34
C(5)	889	219	402	−86	−571	7
C(6)	1335	295	1357	301	1880	457
C(7)	341	572	327	−110	13	−28
C(8)	97	187	534	142	−198	525
C(9)	809	449	486	44	8	−92
C(10)	−350	1226	389	487	149	307
C(11)	1067	362	285	−77	203	−259
C(12)	1207	652	197	7	964	95
C(13)	430	860	751	650	−98	−106
C(14)	−101	978	502	−336	123	112
C(15)	−266	304	334	−199	−174	37
C(16)	1388	271	−16	−11	−517	−94

Table 4. Bond lengths in Å (with standard deviations × 100). Atom numbering according to Fig. 1.

Br −C(1)	1.83(2)
C(1) −C(2)	1.36(3)
C(2) −C(3)	1.53(3)
C(2) −C(16)	1.54(3)
C(3) −C(4)	1.28(4)
C(4) −C(5)	1.48(3)
C(5) −C(6)	1.53(4)
C(6) −C(7)	1.45(4)
C(7) −C(8)	1.38(4)
C(3) −C(8)	1.37(4)
C(8) −C(9)	1.63(4)
C(9) −C(10)	1.48(3)
C(10)−C(11)	1.50(4)
C(11)−C(12)	1.47(3)
C(12)−C(13)	1.34(4)
C(13)−C(14)	1.26(4)
C(14)−C(15)	1.37(4)
C(15)−C(16)	1.41(4)
C(11)−C(16)	1.47(3)

The molecular packing viewed along the *a*-axis is shown in Fig. 2. Only forces of van der Waals type determine the intermolecular packing. There are eight hydrogen-hydrogen distances less than 3 Å per molecule.

It is believed that the effect of this type of tricyclic compounds is due to their ability to inhibit the uptake in the neuronal membrane of nor-

Table 5. Bond angles in degrees (with standard deviations). Atom numbering according to Fig. 1.

Br—C(1) —C(2)	125.7(1.7)
C(1) —C(2) —C(3)	121.2(1.8)
C(1) —C(2) —C(16)	122.1(2.0)
C(3) —C(2) —C(16)	115.6(1.8)
C(2) —C(3) —C(4)	125.0(2.9)
C(2) —C(3) —C(8)	108.8(2.6)
C(4) —C(3) —C(8)	126.1(2.1)
C(3) —C(4) —C(5)	122.3(2.7)
C(4) —C(5) —C(6)	113.7(2.4)
C(5) —C(6) —C(7)	117.8(2.3)
C(6) —C(7) —C(8)	120.6(2.5)
C(7) —C(8) —C(9)	116.5(2.1)
C(7) —C(8) —C(3)	119.5(2.3)
C(3) —C(8) —C(9)	123.9(2.1)
C(8) —C(9) —C(10)	106.6(2.4)
C(9) —C(10)—C(11)	122.5(2.5)
C(10)—C(11)—C(12)	123.9(2.5)
C(10)—C(11)—C(16)	127.3(2.1)
C(16)—C(11)—C(12)	108.0(2.8)
C(11)—C(12)—C(13)	123.9(2.9)
C(12)—C(13)—C(14)	124.2(2.9)
C(13)—C(14)—C(15)	120.6(2.6)
C(14)—C(15)—C(16)	119.3(2.2)
C(15)—C(16)—C(2)	123.5(2.5)
C(15)—C(16)—C(11)	122.7(2.9)
C(11)—C(16)—C(2)	113.4(2.8)

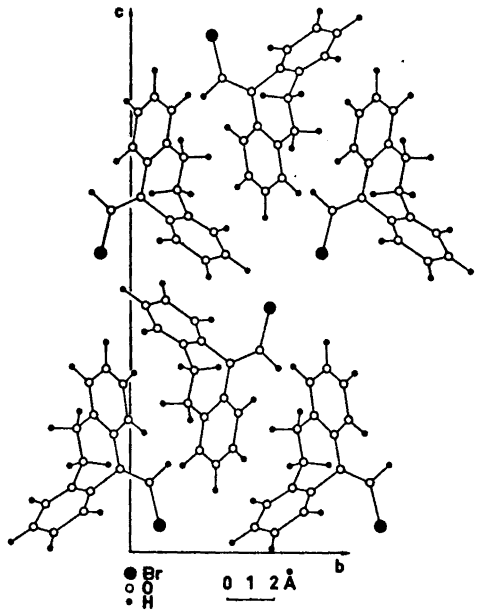


Fig. 2. Molecular packing of 5(bromomethylene)-10,11-dihydro-5H-dibenzo[a,d]-cycloheptene as seen along the *a*-axis.

epinephrine (*cf.* Ref. 6). Furthermore a study of penetration of lipid monolayers by psychoactive drugs indicate that the drug molecules are attached to the lipids of natural membranes. On the assumption that the lipids in the membrane form a bimolecular layer where the chains possess a liquid type of disorder a possible mechanism might be that the rigid skeleton of the drug molecules promote the formation of a more crystalline structure of the lipids and thus reduce the membrane permeability. The present author has started measurements of the effect of this compound with known molecular dimensions on the structure of lipid surface films.

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