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

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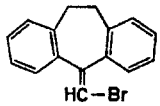
5-(Bromomethylene)-10,11-dihydro-5H-dibenzo[a,d]-cycloheptene has been studied in order to determine the molecular conformation of the pharmacologically active dibenzocycloheptene derivatives. The crystals are orthorhombic with $a=6.270$ Å, $b=9.288$ Å, $c=22.46$ Å. The unit cell contains four molecules, 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.

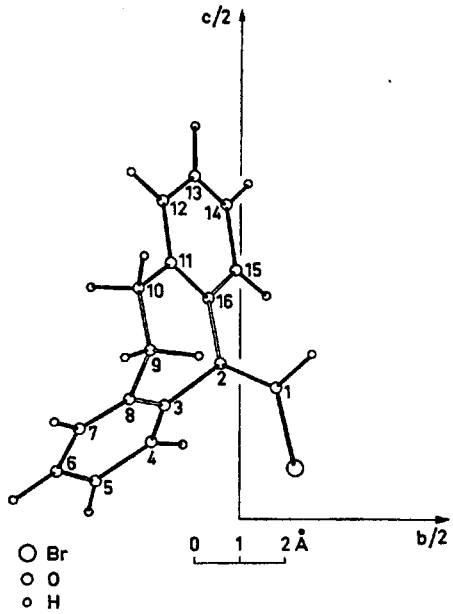


Fig. 1. Stereochemistry of 5-(bromomethylene)-10,11-dihydro-5H-dibenzo[a,d]-cycloheptene.

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	2268	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	3324	3479	0.5000	1	4	7	3299	3127	0.6247
0	0	16	2798	1964	1.0000	0	6	14	2486	2360	0.5000	1	4	8	3817	4192	0.9976
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	6461	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	0.8388
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	2628	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	2355	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	2570	0.5000	1	5	10	3983	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	3312	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	3954	0.9436
0	2	2	3369	2194	0.5000	1	0	2	12366	13490	0.5000	1	6	7	3955	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	13952	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	0.9854
0	2	7	8634	8297	0.5000	1	0	8	3622	4463	0.5000	1	6	21	1707	1892	0.9050
0	2	8	1118	1383	1.0000	1	0	10	4597	4497	0.5000	1	7	0	5633	5096	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	7139	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	2817	1972	0.7480
0	2	16	1714	1332	0.5000	1	1	1	2511	2102	0.1917	1	7	8	4733	4282	0.7979
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	0.9489	1	7	12	2645	2400	0.7646
0	2	20	1310	1112	1.0000	1	1	5	5604	6579	0.8760	1	7	14	2110	2095	0.7945
0	2	25	3329	3212	0.5000	1	1	6	2898	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	3588	3617	0.2963	1	8	4	4057	3874	0.5053
0	3	6	6503	5672	0.7500	1	1	12	5940	5866	0.7644	1	8	6	4291	4217	0.5258
0	3	8	2743	2860	0.7500	1	1	13	2505	3398	0.1987	1	8	7	2830	3074	0.0996
0	3	9	3873	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	2606	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	2141	0.3232
0	3	16	3787	4054	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	1488	0.2500	1	2	1	15171	15180	0.4199	1	9	5	4697	4798	0.7374
0	3	19	1435	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	9081	8620	0.5223	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	10908	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	2357	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	0.0036	2	0	8	3725	3699	1.0000
0	4	11	397	898	0.5000	1	2	12	2263	1664	0.7609	2	0	9	2458	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	3032	0.5000	1	2	14	2688	1939	0.6486	2	0	11	1516	1619	0.7500
0	4	14	2173	2049	1.0000	1	2	17	3536	3283	0.5171	2	0	12	7800	7235	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	9868	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	3561	3668	0.6711
0	5	6	4264	4582	0.7500	1	3	5	4333	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	5912	0.2708	2	1	7	6951	6063	0.2905
0	5	10	2881	2521	0.7500	1	3	9	1411	994	0.7813	2	1	8	4440	2263	0.6918
0	5	11	5854	5770	0.2500	1	3	10	5423	5789	0.1593	2	1	9	5486	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	987	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	3395	3802	0.7500	1	3	14	2447	2461	0.2445	2	1	13	1568	1945	0.1598
0	6	0	2406	1958	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	0.8955
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	1597	0.9584	2	2	1	2368	2318	0.8311

Table 1. Continued.

h	k	l	Fobs	Fcalc	Fi	h	k	l	Fobs	Fcalc	Fi	h	k	l	Fobs	Fcalc	Fi
2	2	2	2198	1356	0.4667	3	1	12	3673	3531	0.2926	4	0	12	4198	3854	0.5000
2	2	3	6948	7257	0.9915	3	1	13	3924	3604	0.8169	4	1	0	2404	2084	1.0000
2	2	4	2460	2150	0.8654	3	1	15	2757	2438	0.7278	4	1	1	3113	3350	0.2520
2	2	5	6556	7563	0.0028	3	2	0	2597	2992	0.7500	4	1	2	3415	2468	0.2082
2	2	6	2132	2365	0.6761	3	2	1	4307	5225	0.0754	4	1	3	2977	2454	0.1877
2	2	7	7011	7197	0.0008	3	2	2	2467	1921	0.8633	4	1	4	4258	3711	0.1445
2	2	8	4276	3760	0.6886	3	2	3	5041	4785	0.9775	4	1	7	3451	3172	0.9207
2	2	9	4649	4453	0.0959	3	2	4	1897	1516	0.7763	4	1	8	3884	2943	0.3641
2	2	10	1784	871	0.8101	3	2	5	2677	2344	0.2091	4	1	9	4875	4320	0.7518
2	2	11	3302	2662	0.5111	3	2	6	1696	1488	0.4401	4	1	10	2630	3259	0.4821
2	2	13	5702	5144	0.5310	3	2	7	4310	3712	0.5431	4	1	11	2198	1962	0.7971
2	2	14	2418	2314	0.1064	3	2	9	4812	4808	0.4950	4	1	12	2594	3028	0.7278
2	2	15	5916	5209	0.4813	3	2	10	1662	1854	0.2290	4	1	13	3224	2794	0.5954
2	2	16	2644	2561	0.0428	3	2	11	4524	4657	0.4763	4	2	0	1589	1397	1.0000
2	2	17	2112	2323	0.5174	3	2	13	3311	3075	0.5416	4	2	1	1416	1616	0.4162
2	3	1	3482	3592	0.8093	3	2	14	2123	1448	0.3040	4	2	2	1352	1490	0.3952
2	3	2	4781	4684	0.3174	3	2	15	2140	2194	0.9271	4	2	3	3739	3301	0.5170
2	3	3	5660	5235	0.8301	3	2	16	2185	1787	0.9802	4	2	4	2191	2249	0.2226
2	3	4	8629	9100	0.2747	3	2	17	2124	1785	0.0820	4	2	5	4541	4230	0.5332
2	3	5	4121	4906	0.2796	3	2	18	2007	1291	0.2845	4	2	6	1796	1974	0.1944
2	3	6	5725	5209	0.2068	3	3	0	7351	7142	0.2500	4	2	7	3359	3009	0.4678
2	3	8	3551	3724	0.1176	3	3	1	2069	2023	0.1379	4	2	9	1935	1298	0.5087
2	3	9	4120	3834	0.3206	3	3	2	4801	4604	0.2348	4	2	10	825	1161	0.5186
2	3	10	2019	1735	0.0916	3	3	3	2348	2432	0.1486	4	2	11	2269	2314	0.9927
2	3	11	1564	2260	0.2750	3	3	4	2006	2532	0.1048	4	2	13	3282	2991	0.8927
2	3	12	3137	3253	0.7347	3	3	5	1974	2944	0.2952	4	3	0	1314	804	1.0000
2	3	13	2762	2219	0.3203	3	3	6	2185	2834	0.8463	4	3	1	2470	1627	0.2297
2	3	14	4184	3373	0.7280	3	3	7	2532	2381	0.2515	4	3	2	2842	3080	0.8527
2	3	16	4474	4997	0.7444	3	3	8	3432	3436	0.8064	4	3	3	1814	1972	0.3741
2	4	0	9304	9769	1.0000	3	3	9	1637	1501	0.4111	4	3	4	4176	3610	0.7338
2	4	2	3863	3194	0.9778	3	3	10	3693	3717	0.7657	4	3	5	1032	1546	0.4794
2	4	3	1999	2355	0.6723	3	3	11	1716	2338	0.6180	4	3	6	2508	2872	0.7688
2	4	4	4271	3573	0.0422	3	3	12	3321	3907	0.6915	4	3	7	2219	2559	0.6660
2	4	5	1686	1472	0.4797	3	3	14	3347	2615	0.6920	4	3	8	2152	1725	0.7165
2	4	6	4446	3919	0.4174	3	3	15	2060	2320	0.6849	4	3	9	1190	1537	0.5625
2	4	7	1372	961	0.5533	3	3	16	2254	2021	0.3779	4	3	10	1737	2263	0.5686
2	4	8	4155	3273	0.5133	3	3	17	2213	2072	0.8907	4	3	11	1786	2621	0.7507
2	4	9	1404	596	0.1601	3	3	18	2109	2355	0.3117	4	3	12	1582	1651	0.4516
2	4	10	6892	5950	0.4585	3	3	20	1825	2253	0.2916	4	3	13	1314	1616	0.9065
2	4	11	3452	3658	0.1134	3	4	0	2119	1170	0.2500	4	3	14	2815	3257	0.3295
2	4	12	5356	5013	0.5071	3	4	1	1792	1743	0.2997	4	3	16	2636	2513	0.2265
2	4	13	3005	2706	0.1415	3	4	2	5366	4233	0.4928	4	4	0	1879	2181	0.5000
2	4	14	1641	2208	0.6265	3	4	3	1565	1065	0.2838	4	4	1	1333	2142	0.1921
2	4	15	1674	1783	0.4884	3	4	4	5841	4658	0.4756	4	4	2	4390	4708	0.5251
2	4	16	1949	2492	0.9703	3	4	5	1642	1898	0.2538	4	4	7	1710	2383	0.8210
2	4	18	1989	2777	0.9592	3	4	6	3664	3679	0.5163	4	4	8	1956	3025	0.0115
2	4	20	1885	2618	0.0214	3	4	7	2200	2577	0.1416	4	4	11	2069	3068	0.5699
2	5	0	1177	1633	1.0000	3	4	8	2129	2463	0.5293	4	4	12	2291	2608	0.0708
2	5	1	6577	6428	0.2367	3	4	9	2267	2625	0.0492	4	5	0	1489	2354	0.5000
2	5	2	3371	2883	0.2655	3	4	10	2120	1369	0.7055	4	5	1	3105	3247	0.7037
2	5	3	3228	3336	0.2482	3	4	12	2129	2401	0.9624	4	5	2	1498	1455	0.6349
2	5	4	2525	2414	0.1591	3	4	13	2172	1683	0.5099	4	5	3	1510	2208	0.7432
2	5	5	1964	1675	0.1687	3	4	14	3605	4218	0.9837	4	5	9	2465	2760	0.3196
2	5	6	2859	3019	0.3151	3	4	15	1720	2047	0.5465	4	5	11	2488	3037	0.2021
2	5	7	4616	4156	0.8162	3	4	16	2221	2662	0.9997	5	0	2	3697	3550	0.5000
2	5	9	7330	6828	0.7746	3	5	0	1631	1628	0.2500	5	0	3	523	106	0.2502
2	5	11	4018	4029	0.7258	3	5	1	1897	1957	0.8036	5	0	4	2852	2910	0.5000
2	5	12	1914	1975	0.8002	3	5	2	2168	2610	0.3354	5	0	5	2024	1640	0.2500
2	5	13	1671	1740	0.7204	3	5	3	3878	3158	0.7846	5	1	0	1660	1890	0.2500
2	6	0	1948	1935	0.5000	3	5	4	2148	1265	0.3078	5	1	1	1953	1603	0.9073
2	6	1	1619	2330	0.3758	3	5	5	5928	5264	0.7899	5	1	2	1512	1365	0.3025
2	6	2	2893	2937	0.3725	3	5	6	2365	2583	0.6259	5	1	3	1965	1190	0.0557
2	6	3	4824	4386	0.4743	3	5	7	5743	5158	0.7424	5	1	4	2807	1789	0.4932
2	6	5	4016	3763	0.5360	3	5	8	1600	1513	0.7877	5	1	5	2843	3212	0.7627
2	6	7	3781	4206	0.5020	3	5	9	2017	1726	0.6198	5	1	6	1952	2817	0.5195
2	6	9	1463	1558	0.5383	3	5	10	2006	2546	0.6851	5	1	7	2083	1699	0.6900
2	6	13	2782	3737	0.9342	3	5	11	2291	2708	0.3738	5	1	9	1694	2061	0.5851
2	6	15	2301	3030	0.9792	3	5	12	1465	1210	0.8045	5	1	10	1762	2715	0.7049
2	7	1	3134	3334	0.1939	3	5	13	2265	2258	0.2224	5	1	11	2279	2418	0.3812
2	7	2	2688	2992	0.8374	3	5	17	2523	3079	0.2762	5	1	12	1571	1504	0.0032
2	7	4	5141	5483	0.7493	3	6	0	1374	1668	0.2500	5	2	1	3643	3009	0.4122
2	7	6	4828	5045	0.7426	3	6	1	5454	4174	0.4285	5	2	2	845	1510	0.2186
2	8	2	3277	4010	0.5713	3	6	3	2336	2567	0.6515	5	2	3	2877	2850	0.6378
2	9	1	3401	3996	0.7078	3	6	4	2579	2564	0.0168	5	2	4	1924	1812	0.0011
3	0	2	4186	4988	1.0000	3	6	5	989	811	0.0059	5	2	5	2098	1624	0.2230
3	0	3	3605	3061	0.7500	3	6	6	1662	1475	0.7464	5	2	6	1442	1624	0.5100
3	0	4	3964	3709	1.0000	3	6	7	1979	1869	0.8248	5	2	7	1948	2049	0.9582
3	0	5	2604	2370	0.7500	3	6	8	1863	1078	0.6491	5	2	8	641	1135	0.8328
3	0	6	5077	4441	1.0000	3	6	9	2296	2805	0.0316	5	2	9	1627	2040	0.9685
3	0	8	6121	5483	1.0000	3	6	11	2870	3710	0.9681	5	2	11	1714	1977	0.9617
3	0	9	1406	702	0.2500	3	6	13	1947	1608	0.0961	5	3	1	812	1681	0.5317
3	0	10	2130	1442	1.0000	3	7	0	2461	2948	0.7500	5	3	2	2604	2259	0.7118
3	0	11	1652	1581	0.7500	3	7	1	1949	1900	0.7068	5	3	3	1571	1978	0.7291
3	0	12	4641	4185	0.5000	3	7	2	3606	4214	0.7593	5	3	4	1054	1323	0.4798
3	0	13	2382	1851	0.2500	3	7	3	2202	2495	0.6824	5	3	5	1398	1239	0.5598
3	0	14	2393	2823	0.5000	3	7	4	1808	1962	0.7422	5	3	6	910	646	0.5773
3	0	15	2502	2680	0.7500	3	7	6	1924	2152	0.3484	5	3	8	2248	2590	0.3512
3	0	16	4233	4416	0.5000	3	7	8	2894	3754	0.2997	5	3	9	1199	1736	0.0014
3	0	17	2599	2971	0.2500	3	7	10	2411	3304	0.2307	5	3	12	2770	2653	0.2678
3	0	18	2645	2681	0.5000	3	7	12	1843	1995	0.2870	5	3	13	1746	2044	0.1622
3	1	0	7491	6915	0.7500	3	8	4	1937	2476	0.9856	5	3	14	1862	1410	0.0434
3	1	1	2900	2131	0.3901	3	8	6	2574	3775	0.0191	5	4	0	1593	1201	0.7500
3	1	2	3495	3054	0.7360	3	8	8	1614	1515	0.9381	5	4	1	1304	861	0.1712
3	1	3	6498	6957	0.2700	4	0	2	1118	1408	1.0000	5	4	2	1735	954	0.9615
3	1	4	2512	1962	0.0187	4	0	3	2807	837	0.7500	5	4	3	662	1579	0.7473
3	1	5	4885	5808	0.2955	4	0	4	2301	2237	1.0000	5	4	4	2012	2224	0.0231
3	1	6	1871	1687	0.1276	4	0	5	1204	1224	0.2500	5	4	5	1798	1462	0.8125
3	1	7	3236	3461	0.1565	4	0	6	2055	2381	0.5000	5	4	6	1824	2485	0.0404
3	1	8	5452	4470	0.1363	4	0	7	911	620	0.7500	5	4	8	706	829	0.0536
3	1	9	2072	2441	0.0989	4	0	8	1832	2180	0.5000						
3	1	10	3303	2912	0.2984	4	0	9	2448	1859	0.2500						
3	1	11	2458	2927	0.8430	4	0	10	2470	2566	0.5000						

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)

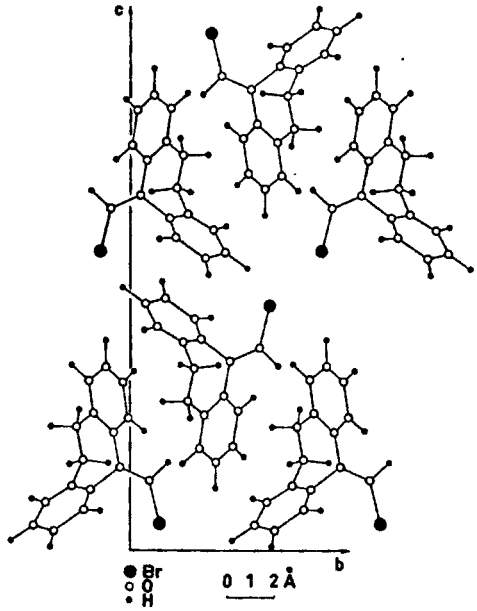


Fig. 2. Molecular packing of 5(bromomethylene)-10,11-dihydro-5H-dibenzo[a,d]-cycloheptene as seen along the *a*-axis.

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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