

Table 5. Intermolecular hydrogen bond dimensions (Å)

Bond X—H···X'	X—X'	X—H	H—X'	Displacement of H from line X—X'	Displacement of X' from molecular plane
O—H(4)···N(2)	2.82	0.77	2.05	0.07	-0.05
N(1)—H(1)···O	3.05	0.94	2.12	0.16	0.90
N(1)—H(2)···N(2)	3.12	0.95	2.23	0.26	0.73

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## The Crystal and Molecular Structure of [3.3]Paracyclophane\*

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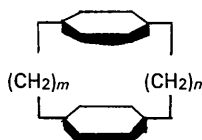
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(Received 24 September 1964)

[3.3]Paracyclophane ( $C_{18}H_{20}$ ) forms monoclinic crystals with  $a_0=9.715$ ,  $b_0=8.138$ ,  $c_0=8.524$  Å,  $\beta=90.69^\circ$ , and two molecules in the unit cell in space group  $P2_1/n$ . The structure has been refined by full-matrix least-squares methods, and the final parameters include small corrections for molecular libration. The aromatic rings are deformed slightly into a symmetrical boat form, the bending being about  $6^\circ$  at each end; the  $\alpha$ -carbons are bent further, by an average of nearly  $4^\circ$ . The two rings do not lie directly above one another, being displaced about 0.5 Å from such an arrangement. The bond angles in the side chain are slightly larger than the normal values, and the dihedral angles are also slightly greater than those in n-butane. All bond distances are consistent with those found in other hydrocarbons. There are no short non-bonded intermolecular contacts, and the shortest intramolecular ones are only slightly less than the sum of the van der Waals radii, and thus are consistent with the comparatively small observed distortion of the molecule. The distribution of the strain energy in this and similar molecules is discussed.

### Introduction

Cram, Allinger & Steinberg (1954) interpreted the ultraviolet absorption spectra of some paracyclophanes,



in terms of (1) trans-annular  $\pi$ -electron interactions between the two benzene rings, and (2) distortion of

the benzene rings from their normal planar configurations. Further evidence for the first of these effects was reported by Cram & Bauer (1959) in their study of the molecular complexes of the paracyclophanes with tetracyanoethylene (TCNE), and significant out-of-plane distortions of the aromatic rings have been found in [2.2]paracyclophane ( $m=n=2$ ) (Brown, 1953a; Lonsdale, Milledge & Rao, 1960; Bekoe & Trueblood, 1964) and in the corresponding diolefin (Coulter & Trueblood, 1963). Similar distortions are observed in the related compounds [2.2]metacyclophane (Brown, 1953b) and 4,12-dimethyl[2.2]metacyclophane (Hanson, 1962). The molecule studied in the present analysis, [3.3]paracyclophane, is of interest not only because, among all the paracyclophanes, it forms the strongest molecular complex with TCNE, but also because it possesses most of the sorts of strains and distortions of the four above-mentioned hydrocarbons,

\* This work was supported in part by the Directorate of Chemical Sciences of the United States Air Force Office of Scientific Research under Contract AF 49(638)-719.

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‡ Contribution No. 1598.

although to a lesser degree. Detailed analyses of the comparative geometries of these and related molecules should be useful in establishing approximate potential functions applicable to these sorts of molecular distortions.

### Experimental

Crystals were supplied by Prof. D. J. Cram and Dr N. L. Allinger. Irregular plates were grown from benzene; for intensity measurements these were cut with a razor blade and then shaped approximately into cylinders, 1–2 mm in length and  $0.25 \pm 0.05$  mm in diameter, by means of tissue paper dampened with isoamyl acetate. Weissenberg photographs with Cu  $K\alpha$  radiation ( $\lambda = 1.5418$  Å) showed the crystals to be monoclinic, with  $a_0 = 9.715$ ,  $b_0 = 8.138$ ,  $c_0 = 8.524$  Å, each  $\pm 0.01$  Å, and  $\beta = 90.69 \pm 0.03^\circ$ . Sodium chloride was used to give a calibration powder pattern ( $a_0 = 5.639$  Å). The systematic extinctions ( $h0l$ ,  $h+l$  odd;  $0k0$ ,  $k$  odd) lead uniquely to the space group  $P2_1/n$ . The observed density (Cram, Allinger & Steinberg, 1954) is  $1.156$  g.cm $^{-3}$ ; that calculated for a two-molecule unit cell is  $1.165$ . Thus the molecule is necessarily centrosymmetric, one half of a molecule, C $_9$ H $_{10}$ , comprising the asymmetric unit.

Multiple-film equi-inclination Weissenberg intensity photographs were taken about the [010] and [101] directions; the appropriate relative film factors were calculated for each layer by taking into account the expected dependence on the equi-inclination angle, but a compromise between these values and the factors observed experimentally for the different layers was used. After reduction of intensities to  $kF^2$  by the usual geometrical factors, the various layers were correlated by a relaxation method (R. A. Sparks, unpublished) which utilized all reflections observed about both axes. Of the 1650 independent reflections in the Cu  $K\alpha$  sphere of reflections, 1480 were accessible; 1095 of these were observed. The maximum error in  $F^2$  due to absorption is calculated to be 5%; no corrections for this effect were made.

The calculations were made on the high-speed computer SWAC (Sparks, Prosen, Kruse & Trueblood, 1956) and on an IBM 709 and a 7090 computer. McWeeny's (1954) form factors for diamond and graphite carbon were used; his hydrogen curve (1951) was also used.

### Determination and refinement of the structure

The  $F^2$  values were modified by division by  $\sum_i f_i^2 e^{-6s^2}$  and multiplication by  $s^4 e^{-19s^2}$  (Waser, 1944), where  $s = \sin \theta / \lambda$ . The modified  $F^2$ 's were used in a three-dimensional Patterson synthesis, the relative scale of the peaks being established from the height of the origin peak. This sharpened Patterson map was interpreted with the help of an idealized molecular model in which only the central atom of each three-carbon bridge was omitted (because its position was least easy to surmise). Most of the vectors corresponding to one

aromatic ring and its two attached methylene carbons were identified; they were nearly, although not quite, coplanar and were used to orient the molecule about the center of symmetry. The direction cosines of these vectors were used in the calculation of the normal to the least-squares plane formed by the vectors. This normal made an angle of about  $14^\circ$  with a strong Patterson vector (about  $3.3$  Å long) which seemed quite clearly to arise from the parallel inter-ring interactions between the six carbons of one benzene nucleus and those of the other. The magnitude of this angle suggested that the aromatic rings were displaced significantly relative to one another, and indeed this was later found to be so (Fig. 4). However, in order to avoid the necessity of a trial model containing this sort of parallel displacement, it was assumed at this stage that the normal and the shortest inter-ring vector were parallel, an average of the two vectors cited above being used. Approximate positions were thus deduced for eight of the nine unique carbon atoms (all but the central bridge atom), and these positions were used in the calculation of phases for a three-dimensional Fourier synthesis. These eight atoms appeared in the synthesis as peaks of height within ten per cent of  $6$  e.Å $^{-3}$ ; the ninth carbon appeared as a peak of height  $4$  e.Å $^{-3}$ , at just the expected position. No other peaks above  $1$  e.Å $^{-3}$  were present; thus it appeared that the trial structure was correct.

In the initial least-squares refinement, only the 905 observed reflections with  $\sin \theta$  greater than  $0.5$  were used, in order to minimize any effects arising from neglect of the hydrogen atoms. The full-matrix least-squares program used was that described by Sparks *et al.* (1956); the weighting system was that of Hughes (1941) with  $4F_{\min}$  taken as  $3.2$ . Because of limitations in the size of the memory of the computer SWAC, it was not possible to refine 9 parameters for each atom simultaneously. Instead the refinement was done in three stages, with six parameters for each atom and an overall scale factor refined in each stage. In the first stage the six parameters were the three position parameters and three  $B_{ii}$  terms of the temperature factor ellipsoid for each atom; in the second stage the six temperature factor parameters for each atom were

Table 1. *Hydrogen atom positions and peak heights\**

Atom	$10^3 x$	$10^3 y$	$10^3 z$	Peak height, e.Å $^{-3} \times 10^2$
1	104	062	296	44
2	-110	-074	273	40
4	036	-342	-094	39
5	266	-206	-053	37
7a	318	139	206	40
7b	395	-002	097	49
8a	402	225	-038	39
8b	318	095	-132	38
9a	202	363	056	40
9b	230	367	-121	32

\* In difference Fourier synthesis calculated after refinement of carbon parameters (see text). Atom numbers are the same as those of the attached carbon atoms.



Table 2 (cont.)

-4	4.6	-4.4	4	5.3	4.9	-6	2.9	2.8	H	3.5	3.2	-8	1.5	1.2	0	0.6U	-1.1	-5	0.4U	0.3	5	1.9	-1.6	
-3	7.0	-7.0	3	3.7	-3.9	-5	1.3	1.2	H	7. K	3	-6	0.7	-1.0	1	0.6U	-0.6	-4	0.6U	0.1	H	10. K	4	
-2	1.3	1.2	6	7.8	7.8	-4	3.9	4.2	-8	0.6U	-0.3	-4	3.5	3.4	2	0.6U	0.1	-3	2.3	-2.4	-5	1.3	1.3	
-1	0.9	-1	5	0.6U	0.1	2	3.8	3.8	-2	1.9	-0.2	-2	1.2	1.2	3	0.6U	0.1	-2	2.3	2.4	0.4U	0.4		
0	6.6	6.6	8	6.6	7.1	-2	6.6	7.2	-6	0.6U	-0.8	U	20.9	-21.8	4	0.6U	0.5	-1	2.2	-2.1	-3	2.0	2.7	
1	2.7	2.6	9	1.1	-1.1	-1	5.3	5.7	-5	6.2	-6.3	2	6.1	-6.5	5	0.4U	0.6	0	1.2	-1.4	-2	1.3	-1.3	
2	1.4	1.2	H	6. K	2	0	2.1	2.3	-4	0.7U	-0.2	4	3.9	-3.6	H	6	2.1	2	2.6	-2.6	-1	0.7	-0.8	
3	8.5	8.5	-9	1.0	-1.1	1	1.0	1.0	-3	0.7U	-1.2	6	3.5	3.6	H	7. K	6	2	2.5	2.3	U	0.6U	0.4	
4	2.8	2.8	-1	0.6U	0.1	2	3.8	3.8	-2	2.5	2.7	8	5.2	-5.2	-5	0.4U	0.6	3	2.3	-2.4	1	1.7	1.7	
5	3.6	3.6	-7	0.6U	0.1	3	2.5	2.2	-1	1.9	-1.5	H	8. K	1	-4	1.7	-1.9	4	0.6U	0.3	2	4.7	-3.8	
6	0.7	0.6	-6	3.1	-3.0	4	1.9	1.4	U	5.3	-5.1	-8	0.8	1.0	-3	0.6U	-0.0	5	0.4U	0.4	3	4.6	4.3	
7	0.6U	-0.1	-5	4.8	-4.9	5	2.1	-2.0	1	3.9	-3.6	7	0.6U	0.3	-2	0.6U	-0.2	6	0.4U	1.0	4	0.4U	-3.5	
8	2.7	2.3	-4	2.6	-2.6	6	0.6U	0.0	2	4.0	-3.6	-6	3.2	3.4	-1	0.6U	-0.6	H	9. K	5	H	10. K	5	
H	5. K	6	-3	3.3	3.1	7	0.4U	0.0	3	2.0	2.2	-5	1.1	1.2	C	0.6U	0.7	-5	0.4U	0.0	-4	1.9	1.9	
-7	2.2	2.1	-2	8.7	8.1	H	6. K	7	4	3.8	-3.6	-4	5.6	5.9	1	2.0	-2.2	-4	0.4U	-0.1	-3	0.4U	-0.8	
-6	3.8	3.7	-1	7.3	6.6	-6	0.4U	-0.5	5	4.0	-4.0	-3	3.8	3.9	2	1.9	-1.0	-3	2.6	2.4	-2	0.4U	0.4	
-5	1.5	1.2	0	0.6U	-0.4	-5	1.3	-1.1	6	1.8	1.6	-2	10.2	10.3	3	0.6	-0.9	2	0.7	-1.3	-1	0.4U	0.4	
-4	1.5	-1.3	1	7.0	6.0	-4	3.1	-3.7	7	0.6U	0.0	-1	12.4	-13.2	4	3.0	-2.7	-1	0.6U	-0.0	0	0.4U	-0.8	
-3	4.9	4.8	2	2.7	-2.4	3	1.2	1.1	8	0.4U	0.3	0	1.6	1.7	5	0.7	0.8	0	0.6U	-1.0	1	1.3	-1.0	
-2	6.8	-6.5	3	5.5	5.0	-2	0.6U	-0.8	H	7. K	4	1	0.8U	-0.7	H	8. K	7	1	1.4	-1.0	2	1.6	1.6	
-1	3.8	3.3	4	13.5	-13.5	-1	1.5	-1.5	-8	0.4U	-0.3	2	0.8U	0.2	-4	0.4U	1.0	2	2.5	-2.4	3	0.4U	0.1	
0	2.1	-1.6	5	4.2	-3.8	0	3.9	4.0	-7	2.0	1.8	3	0.9U	-0.0	-3	0.4U	0.1	3	1.5	-1.3	H	10. K	6	
1	2.8	-2.8	6	1.4	-1.3	1	0.7U	0.1	-6	0.6U	-0.3	4	2.9	-3.0	-2	0.6U	0.8	4	1.3	1.2	-1	1.8	-1.5	
2	5.5	-5.8	7	2.3	3.9	2	0.7U	0.2	-5	0.6U	-0.7	5	3.8	3.8	-1	0.6U	0.9	5	0.6U	-0.3	0	1.9	1.7	
3	0.6U	-0.2	8	1.5	1.4	3	0.8U	0.5	-4	1.3	-1.0	6	0.8U	-0.9	0	0.6U	0.1	H	9. K	6	H	10. K	7	
4	0.9	0.7	9	0.4U	0.8	H	6. K	8	-3	0.7	-1.0	7	0.6U	-0.8	1	0.6U	0.7	-4	1.5	1.5	H	11. K	0.1	
5	2.7	-2.5	H	9. K	3	0	0.4U	0.3	3	3.4	3.4	H	8. K	2	H	0	2.4	2.4	-2	1.8	1.6	-5	0.4U	0.2
6	1.9	1.9	-8	0.6U	-0.2	-3	1.8	-2.1	-1	3.8	-3.5	H	8. K	1	H	0	2.4	2.4	-2	0.4U	0.0	-3	1.3	1.3
7	1.9	1.9	-8	0.6U	0.2	-2	4.0	-4.4	U	2.0	-2.0	-8	0.4U	0.4	H	9. K	0	-1	2.2	2.1	-1	2.5	-2.5	
H	5. K	7	-7	2.5	-2.4	-1	3.5	3.5	1	4.7	-5.1	-7	2.6	2.6	-7	1.1	1.3	0	1.6	-1.3	1	2.3	-2.2	
-6	1.3	-1.3	-6	4.5	-4.4	U	4.5	-4.5	2	2.5	-2.2	-6	0.6U	0.1	-5	1.0	0.0	1	0.4U	0.0	3	2.4	-2.4	
-5	0.9	0.8	-5	0.1	-0.1	1	1.6	1.6	3	0.6U	-0.3	-3	0.6U	-0.3	-3	0.7U	-2.3	3	2.3	-1.9	H	11. K	1	
-4	1.7	1.8	-4	7.9	-8.4	2	0.6U	-1.2	4	3.1	-2.8	-4	5.6	6.2	-1	8.6	-9.0	3	1.6	-1.1	-5	0.4U	-0.8	
-3	6.8	-6.9	-3	5.7	-5.7	3	2.7	2.7	5	0.6U	0.5	-3	4.7	4.5	1	3.8	4.1	4	2.3	-2.2	-4	1.9	1.9	
-2	4.3	4.0	-2	2.6	2.7	H	6. K	9	6	0.9	-1.3	-2	4.1	4.1	3	3.8	-4.0	H	9. K	7	-3	0.6U	-0.8	
-1	1.1	1.3	-1	3.7	-3.1	-1	3.4	-3.3	7	0.4U	0.5	-1	0.7U	0.6	5	4.2	-4.1	-2	2.2	2.1	-2	0.7U	0.7	
0	0.6U	0.5	9	0.4U	0.5	U	0.4U	0.3	8	0.4	0.3	0	4.6	4.6	-7	0.2	0.0	-6	0.6U	-0.2	0	0.6U	-0.7	
1	0.7U	-1.2	1	5.0	-4.7	1	0.4U	0.0	H	7. K	5	1	3.5	-2.8	H	9. K	1	H	10. K	0	0	0.7U	-0.6	
2	0.8U	-1.2	2	3.6	3.5	H	7. K	0	-7	1.0	-0.6	2	9.4	9.4	-7	1.6	-1.4	-6	4.2	-3.8	1	0.7U	-1.5	
3	0.7U	0.3	3	1.3	-1.1	-9	0.4U	-0.4	-6	2.5	2.4	3	1.9	2.0	-6	0.6U	-0.3	-4	0.6U	0.2	2	2.4	-2.3	
4	2.5	-2.6	5	4.2	-8.1	-7	2.8	-2.7	5	1.6	1.8	-5	0.6U	-0.2	-3	0.6U	-0.2	3	2.3	-1.9	3	1.1	1.1	
H	5. K	8	5	4.1	-4.1	-5	4.6	-5.2	-4	0.6U	0.1	6	2.9	-2.7	-4	0.9	1.0	C	3.8	3.9	4	0.6U	0.0	
-5	1.4	-1.2	6	7.4	-7.3	-3	3.6	3.6	-3	3.4	3.6	6	3.5	3.4	-3	3.1	3.1	2	0.6U	0.7	H	11. K	2	
-4	0.6	-1.1	7	2.4	2.4	-1	13.5	-14.0	-2	2.5	2.6	7	1.5	1.6	-1	4.2	4.0	4	3.3	-3.2	-4	0.4U	-0.7	
-3	0.6U	-0.3	8	0.6U	-0.3	1	4.3	-4.4	-1	4.4	4.5	8	2.5	-2.4	0	2.2	1.9	6	1.7	1.6	-3	0.6U	1.0	
-2	0.6U	0.5	9	0.4U	0.1	3	5.8	-4.9	0	0.7U	0.0	0.8	H	8. K	3	1	1.4	1.2	H	10. K	1	-2	0.6U	1.1
-1	3.1	-3.1	H	6. K	4	5	7.2	7.0	1	2.4	-2.5	-7	0.4U	0.8	2	5.9	6.1	-6	2.4	-2.0	-1	1.1	1.3	
0	5.2	4.9	-8	0.4U	-0.3	7	7.3	6.8	2	4.2	3.9	-6	0.6U	-0.9	3	1.3	1.6	-5	1.9	-2.0	0	0.6U	-0.0	
1	0.7	-0.9	-7	1.8	1.8	H	7. K	1	3	1.4	-1.0	-5	1.7	1.9	4	2.0	-2.0	-4	3.3	-3.6	1	0.6U	0.7	
2	2.0	1.8	-6	0.6U	0.1	-9	0.4U	0.6	4	2.7	2.5	-4	4.6	-4.9	5	0.7U	-1.3	-3	0.7U	0.8	2	1.6	1.7	
3	0.6U	-1.5	-7	3.1	-3.3	-8	0.6U	-0.3	5	0.6U	0.1	6	3.5	3.5	6	0.7U	-0.9	-2	2.2	-2.1	3	0.9	-1.2	
4	3.4	3.2	-4	7.5	-7.9	-7	3.9	3.7	6	0.4U	-0.4	-2	0.7U	-1.0	7	0.6U	1.0	-1	1.2	0.6	4	0.7	-1.1	
H	5. K	9	-3	4.1	-4.1	-6	4.1	-4.5	H	7. K	6	0	4.8	-5.1	-7	1.0	1.0	0	4.8	-4.9	H	11. K	3	
-3	0.8	0.9	-2	2.0	-1.9	-5	3.4	3.4	H	7. K	6	0	4.8	-5.1	-7	1.0	1.0	1	4.6	4.2	-4	0.4U	-0.2	
-2	2.0	-2.1	-1	2.5	-2.4	-4	5.0	-5.1	-6	0.4U	-0.0	1	3.0	2.8	-6	0.6U	-0.8	2	1.6	-1.4	-3	0.4U	-0.5	
-1	2.7	2.8	-1	0.6U	-0.7	8	3.3	8.4	-5	0.6U	-1.3	2	3.6	3.6	-3	0.6U	-1.0	3	2.3	-1.9	-2	0.9	-0.7	
0	1.3	-0.8	1	0.6U	-0.8	-2	5.5	5.4	-4	0.6U	-0.1	3	2.1	2.2	-4	1.6	-1.5	4	0.6U	-0.7	-1	0.6U	-0.0	
1	0.4U	-0.2	2	0.6U	0.8	-1	0.9	1.2	-3	0.6U	-0.5	4	0.7U	0.7	-3	1.6	-1.3	5	0.6U	-0.1	C	1.7	2.0	
2	0.6U	0.2	3	3.2	-3.2	0	3.4	-3.4	-2	1.8	1.7	5	2.9	2.8	-2	3.3	3.3	6	0.4U	-0.2	1	2.7	2.7	
3	1.0	1.2	4	2.7	2.3	1	3.3	-6.0	-1	6.0	1.1	6	1.6	1.6	-1	0.7	-0.6	H	10. K	2	2	1.5	-1.4	
H	6. K	0	5	7.5	-7.5	2	0.8U	-0.1	0	0.9	1.0	7	0.6U	-0.3	0	3.7	-3.5	-6	0.4U	-0.8	3	1.4	3.4	
-6	3.6	3.7	6	0.6U	0.9	3	0.8U	-0.4	1	3.6	3.7	H	8. K	4	1	10.0	10.3	-5	1.4	-1.4	H	11. K	4	
-5	2.1	-2.3	7	0.6U	0.5	4	4.9	-4.7	2	2.4	-2.4	-7	0.4U	-0.4	2	0.7U	0.2	-4	0.7	0.3	-3	2.0	-1.3	
-4	0.6U	-0.6	8	1.0	0.8	5	0.9U	1.1	3	3.1	3.4	-6	0.7	1.0	3	3.8	4.2	-3	0.6U	-0.6	-2	2.6	-2.1	
-3	2.9	2.8	H	5. K	5	6	7.5	7.7	4	1.4	1.6	-5	1.0	-1.0	-2	1.3	-1.1	-2	0.7U	-0.6	-1	0.4U	0.7	
U	8.9	8.5	-8	0.8	0.9	7	6.9	6.9	5	0.4U	-0.4	-6	0.6U	-0.4	5	1.7	1.7	-1	3.9	-3.8	U	0.4U	-0.4	
2																								

same as that used in the SWAC refinements. In addition to nine parameters for each carbon atom and an overall scale factor, the position parameters and an isotropic thermal parameter were refined for each hydrogen atom. The unobserved reflections were included with  $F_o = F_{\min}/\sqrt{3}$ , where  $F_{\min}$  is the appropriate minimum observable structure factor in that region of reciprocal space (Hamilton, 1955). This is the value listed for such a reflection in Table 2; they are identified by the letter U. Convergence was achieved in three cycles; the largest shift for any parameter in the final cycle was  $0.2\sigma$ , where  $\sigma$  is the standard deviation estimated from the inverse of the matrix of the least-squares normal equations. The final discrepancy index,  $R$ , was 0.127 for all accessible data and 0.111 for the observed reflections only; if the fifteen strongest reflections are omitted, the corresponding values are 0.090 and 0.070. A difference Fourier synthesis calculated with phases based on the final parameters contained no density outside the range  $-0.19$  to  $+0.17$  e.Å<sup>-3</sup>, fluctuations not inconsistent with the e.s.d. of the electron density, about 0.06 e.Å<sup>-3</sup> (Cruickshank, 1949). The calculated structure factors were greater than the estimated minimum observable value for about ten per cent of the 385 reflections which were too weak to be measured, but of these, only three were greater than  $1.5 F_{\min}$  (5,2,7, 1.7  $F_{\min}$ ; 3,10,1, 1.8  $F_{\min}$ ; 4,1,10, 3  $F_{\min}$ ).

The final position parameters, with their approximate e.s.d.'s, are given in Table 3 and the final individual temperature factors in Table 4. The anisotropic thermal parameters of the carbon atoms were used in a determination of the translational and librational tensors for the molecule considered as a rigid body (Cruickshank, 1956a, b). The results are given in Table 5; the fit was rather good, the r.m.s. discrepancy between the observed and derived  $U_{ii}$  and  $U_{ij}$  being only about 5% of the average  $U_{ii}$ , with the largest discrepancy only 12%.

### Crystal and molecular structure

A small portion of the molecular arrangement in the crystal is depicted in Fig. 1, and the closest intermolecular approaches are given in Table 6. There are no

intermolecular C...C distances as small as 3.5 Å; the shortest C...H and H...H contacts are 2.9 and 2.5 Å respectively, which are approximately the sums of the accepted van der Waals radii. One of the

Table 3. Final position parameters\*†

Atom	Before libration correction‡			After libration correction		
	x	y	z	x	y	z
C(1)	0890	-0273	2167	0892	-0274	2171
C(2)	-0339	-1111	2043	-0341	-1114	2047
C(3)	-0578	-2253	0859	-0580	-2258	0861
C(4)	0537	-2664	-0068	0537	-2670	-0069
C(5)	1775	-1842	0071	1779	-1846	0071
C(6)	1949	-0556	1124	1953	-0557	1126
C(7)	3165	0582	1054	3172	0585	1056
C(8)	3159	1692	-0401	3166	1697	-0402
C(9)	2000	2945	-0535	2005	2952	-0536
H(1)	104	065	289	104	065	289
H(2)	-105	-081	279	-105	-082	280
H(4)	036	-350	-088	036	-351	-088
H(5)	264	-205	-064	265	-206	-064
H(7a)	321	132	204	321	132	204
H(7b)	395	-005	104	396	-005	105
H(8a)	399	225	-037	400	226	-038
H(8b)	321	090	-139	322	090	-139
H(9a)	198	361	047	199	361	047
H(9b)	225	363	-128	225	364	-128

\* Carbon parameters  $\times 10^4$ ; hydrogen parameters  $\times 10^3$ .

† For the carbon atoms,  $a_0 \sigma(x) = b_0 \sigma(y) = c_0 \sigma(z) = 0.0025 - 0.003$  Å; for the hydrogen atoms, the e.s.d.'s were also approximately isotropic and equal to 0.03–0.04 Å.

‡ For details of the libration correction, see text and Table 5.

Table 4. Final temperature factor parameters\*†

	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$		$B$
C(1)	132	167	132	44	-36	-15	H(1)	3.5 Å <sup>2</sup>
C(2)	125	167	144	36	5	7	H(2)	4.5
C(3)	137	141	144	9	-32	37	H(4)	3.9
C(4)	159	142	140	25	-13	-5	H(5)	4.4
C(5)	138	173	150	51	8	6	H(7a)	6.0
C(6)	114	167	142	24	-37	23	H(7b)	5.4
C(7)	109	224	185	2	-42	-1	H(8a)	4.5
C(8)	112	226	194	-65	16	-2	H(8b)	5.3
C(9)	152	177	193	-71	-27	43	H(9a)	4.9
							H(9b)	6.2

\* Carbon values (dimensionless)  $\times 10^4$ .

† For carbons  $\sigma(B_{ii}) = 3 - 6 \times 10^{-4}$  and  $\sigma(B_{ij}) = 5 - 9 \times 10^{-4}$ ; for hydrogens,  $\sigma(B) = 0.7 - 0.9$  Å<sup>2</sup>.

Table 5. Rigid-body translational and librational tensors\*

$$\mathbf{T} = \begin{pmatrix} 0.054 & 0.003 & -0.003 \\ & 0.046 & 0.000 \\ & & 0.047 \end{pmatrix} \text{Å}^2 \quad \boldsymbol{\omega} = \begin{pmatrix} 6 & -2 & 1 \\ & 6 & -0 \\ & & 11 \end{pmatrix} (^\circ)^2$$

Principal axes:	Eigenvalue	Direction cosines of eigenvector		
$\mathbf{T}$	0.056 Å <sup>2</sup>	0.906,	0.298,	-0.302
	0.047	0.043,	0.643,	0.764
	0.044	0.422,	-0.705,	0.570
$\boldsymbol{\omega}$	11 (°) <sup>2</sup>	0.281,	-0.180,	0.943
	8	-0.608,	0.727,	0.320
	4	0.742,	0.663,	-0.095

\*  $\langle \sigma(\mathbf{T}) \rangle$  is about 0.002 Å<sup>2</sup> and  $\langle \sigma(\boldsymbol{\omega}) \rangle$  is about 1 (°)<sup>2</sup>. The reference axes are  $\mathbf{a}$ ,  $\mathbf{b}$ , and  $\mathbf{c}^*$ . The values given here are for the molecule centered at the origin.

hydrogen atoms on C(7) lies nearly on the axis of one of the aromatic rings of an adjacent molecule and is essentially 'in contact' with these aromatic carbons, a situation found in other structures, for example, diphenylene (Waser & Lu, 1944) and 4-nitroaniline (Trueblood, Goldish & Donohue, 1961). The rigid body motion of the molecule (Table 5) is not large and bears no obvious relation to the packing arrangement or the molecular axes of Table 7. The translational motion is reasonably isotropic, and although the r.m.s. amplitudes of libration vary from  $2^\circ$  to a little over  $3^\circ$ , these values are small and their uncertainties are sufficient that the moderate anisotropy is of doubtful significance. It might seem plausible to speculate that the librational motion would be governed by the nestling of H(7a) in the 'depression' in the aromatic ring of molecule *B* (Table 6) and thus that the molecule would pivot about the line between H(7a) and its centrosymmetric counterpart. However, the necessary coupling of motions of adjacent molecules implied by this sort of libration makes it unlikely, and in fact the r.m.s. amplitude of libration about this direction is only about  $2.6^\circ$ . Presumably the other contacts listed in Table 6 also effectively restrict this motion.

The packing does appear rather efficient, but there are no intermolecular contacts so close that they should give rise to appreciable distortions of the molecule, and thus the major distortions which do exist must be ascribed to intramolecular effects. The geometry of the [3.3]paracyclophane molecule in the crystalline state is illustrated in Figs. 2, 3, 4 and 5. For simplicity, the hydrogen atoms have been omitted from most of these drawings; however, the distances and angles involving them have been included in the summarizing tables (Tables 8 and 9). The aromatic rings are bent out of

the planar conformation, although the deformation angle,  $\alpha$  (Fig. 3), is only about half as large as in the corresponding [2.2] compound and its diolefin. Similarly, the greater length of the bridges between the rings here has reduced  $\beta$ , the angle of bending of the exocyclic C-C bonds out of the plane, by a factor of three to four relative to the [2.2] compounds. The difference in  $\beta$  at the two ends of the molecule (Fig. 3) is real and is related to the parallel displacement of the rings evident in Fig. 4, which is a view down axis *B* of Table

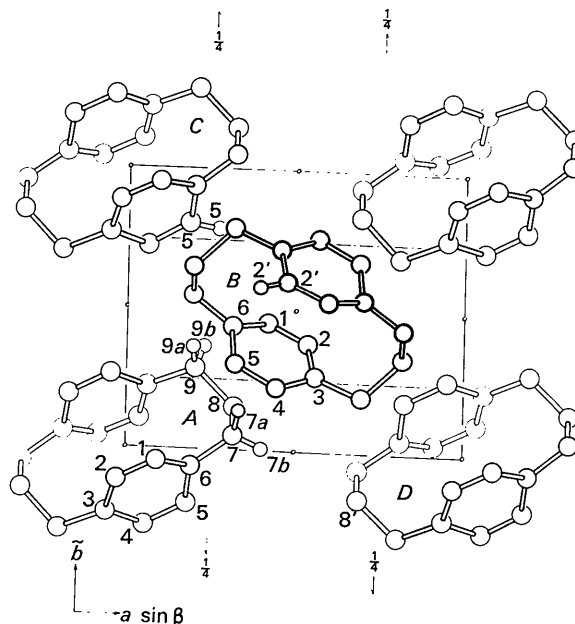


Fig. 1. A portion of the molecular arrangement in the crystal. The numbered atoms are those referred to in Table 6.

Table 6. Shortest C...H and H...H intermolecular distances\*†

H(7a) ( <i>A</i> ) ... C(1) ( <i>B</i> )	2.98 Å	H(9a) ( <i>A</i> ) ... C(1) ( <i>B</i> )	3.01 Å
... C(2) ( <i>B</i> )	3.04	... C(6) ( <i>B</i> )	3.15
... C(3) ( <i>B</i> )	3.12	H(7b) ( <i>A</i> ) ... C(8') ( <i>D</i> )	3.16
... C(4) ( <i>B</i> )	2.96	H(5) ( <i>C</i> ) ... C(2') ( <i>B</i> <sub>-1</sub> )	3.17
... C(5) ( <i>B</i> )	2.88	... H(2') ( <i>B</i> <sub>-1</sub> )	2.54
... C(6) ( <i>B</i> )	2.99	H(9b) ( <i>A</i> ) ... H(2') ( <i>B</i> <sub>-1</sub> )	2.56

\* Molecules *A*, *B*, *C* and *D* are shown in Fig. 1. The reference asymmetric unit (at *x*, *y*, *z*) is related to the symbols in the above table by:

$$\begin{aligned} B &\text{ at } (\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z) \\ B_{-1} &\text{ at } (\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z) \\ C &\text{ at } (x, 1+y, z) \\ D &\text{ at } (1+x, y, z) \end{aligned}$$

with primed atoms of a given molecule related to the corresponding unprimed by the molecular center of symmetry.

† All C...C less than 3.5 Å, C...H less than 3.2 Å, and H...H less than 2.6 Å are given.

Table 7. Approximate molecular axes\*

Axis	Direction cosines†	Description
<i>A</i>	0.868, 0.489, 0.080	Longest molecular axis [C(3)–C(6) direction]
<i>B</i>	–0.328, 0.688, –0.648	Normal to plane of C(1), C(2), C(4), C(5)
<i>C</i>	0.372, –0.537, –0.758	Normal to axes <i>A</i> and <i>B</i> , and approximately parallel to C(1) ... C(5) and C(2) ... C(4) directions

\* These axes are mutually orthogonal

† With respect to the directions of *a*, *b*, *c*\* respectively; the values given are for the molecule centered at the origin.

Table 8. Bond distances and bond angles\*†‡

1-2	1.382 Å	6-1-2	121.2°	6-1-H(1)	115°
2-3	1.392	1-2-3	121.6	2-1-H(1)	123
3-4	1.392	3-4-5	121.3	1-2-H(2)	117
4-5	1.384	4-5-6	121.4	3-2-H(2)	122
5-6	1.391			2-4-H(4)	116
6-1	1.390	2-3-4	116.7	5-4-H(4)	123
		5-6-1	117.0	4-5-H(5)	125
6-7	1.507			6-5-H(5)	114
9-3'	1.517	2-3-9'	121.7		
		4-3-9'	121.5	6-7-H(7a)	110
7-8	1.537	1-6-7	120.8	6-7-H(7b)	108
8-9	1.525	5-6-7	121.9	8-7-H(7a)	108
				8-7-H(7b)	108
1-H(1)	0.98	6-7-8	113.6	7-8-H(8a)	106
2-H(2)	0.98	7-8-9	116.8	7-8-H(8b)	106
4-H(4)	0.98	8-9-3'	115.9	9-8-H(8a)	109
5-H(5)	1.06			9-8-H(8b)	113
7-H(7a)	1.04			8-9-H(9a)	108
7-H(7b)	0.92			8-9-H(9b)	106
8-H(8a)	0.93			3'-9-H(9a)	109
8-H(8b)	1.06			3'-9-H(9b)	111
9-H(9a)	1.01				
9-H(9b)	0.88			H(7a)-7-H(7b)	108
				H(8a)-8-H(8b)	105
				H(9a)-9-H(9b)	106

\* Carbon atoms are identified merely by their numbers. Hydrogen atom numbers are the same as those of the carbon to which the hydrogen is bonded.

† Corrected for librational effects; for most bond distances, this resulted in an increase of about 0.003 Å.

‡ Approximate e.s.d.'s: C-C, 0.004 Å; C-H, 0.04 Å; C-C-C angles 0.3°; C-C-H, 3°; H-C-H, 5°.

7. The fact that the C-C-C angle at C(9) is more than 2° larger than that at C(7) is also related to the displacement of the rings. These effects, together with the increase in the C(7)-C(8)-C(9) angle to nearly 117°, some 5° greater than its normal value (Bonham & Bartell, 1959), are the results of non-bonded intramolecular C...C repulsions (Fig. 5).

The dihedral angles in the trimethylene bridge are 65° (6-7-8-9) and 70° (7-8-9-3'), and thus the con-

formation is similar to that in *gauche* n-butane, where the angle is 63° (Bonham & Bartell, 1959). In view of the sensitivity of these dihedral angles to an increase in the C(6)-C(3') distance while bond distances and angles remain constant, the average increase of only 5° might appear surprisingly small. However, repulsion between C(8) and two of the aromatic ring carbons, C(5) and C(2') (Fig. 5), acts as a constraint on further increases. In fact, C(5) and C(2) are displaced by 0.010 Å (Table 10) relative to C(1) and C(4) in the direction normal to the least-squares plane of all four atoms

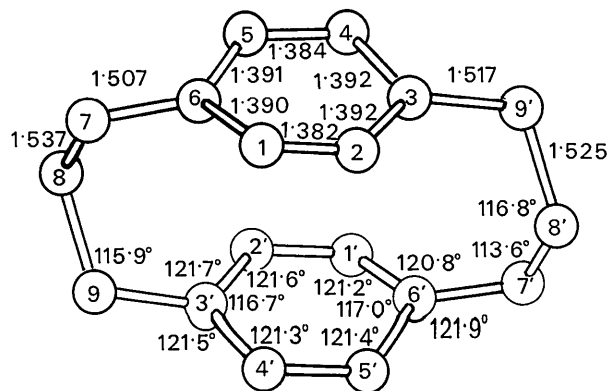


Fig. 2. Bond distances and angles (after librational corrections).

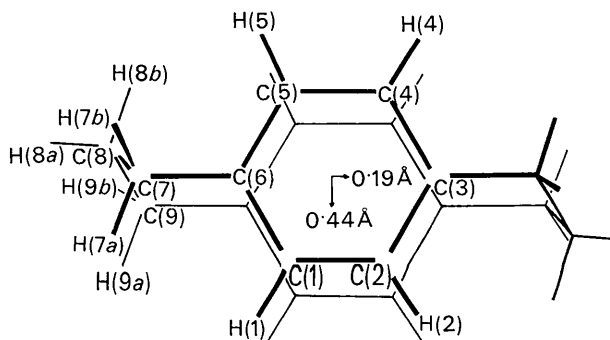


Fig. 4. View of the molecule along the normal to the plane of the aromatic rings (Axis B of Table 7).



Fig. 3. Out-of-plane distortion of the aromatic rings.

Table 9. Some non-bonded intramolecular distances and angles\*†

H(8b)-2'	2.85 Å	1-5	2.37 Å	4-2-5'	97.3°
H(8b)-5	2.92	2-4	2.37	5-1-4'	97.8
8-H(2')	2.97	3-1	2.42	1-2-5'	92.4
8-H(5)	3.10	3-5	2.42	5-4-1'	93.2
		6-2	2.42		
		6-4	2.42		
H(8b)-H(2')	2.41	7-1	2.52		
H(8b)-H(5)	2.55	7-5	2.53		
		7-9	2.61		
1-4	2.75	9-2'	2.54		
2-5	2.74	9-4'	2.54		
3-6	2.83	8-3'	2.58		
		8-6	2.55		

\* All carbon-carbon distances smaller than 3.5 Å which are not shown in Fig. 5 are listed here. H...H distances smaller than 2.6 Å and with at least four intervening bonded carbon atoms and C...H distances less than 3.2 Å and with at least three intervening bonded carbon atoms are shown. All distances have been corrected for librational effects.

† Carbon atoms are identified merely by their numbers.

Table 10. Some least-squares planes\*†

	Plane		
	I	II	III
$l_1$	-0.3273	-0.3538	-0.3002
$l_2$	0.6881	0.7225	0.6501
$l_3$	-0.6476	-0.5940	-0.6980
$D(\text{Å})$	1.633	1.563	1.533
	Deviations of atoms (Å)		
C(1)	<b>0.005</b>	<b>0.004</b>	-0.157
C(2)	<b>-0.005</b>	<b>-0.004</b>	-0.169
C(3)	0.081	<b>0.002</b>	<b>-0.002</b>
C(4)	<b>0.005</b>	-0.157	<b>0.005</b>
C(5)	<b>-0.005</b>	-0.170	<b>-0.005</b>
C(6)	0.083	<b>-0.002</b>	<b>0.002</b>
C(7)	0.373	0.286	0.292
C(9')	0.324	0.247	0.239
H(1)	0.08	0.14	-0.14
H(2)	-0.03	0.03	-0.25
H(4)	0.04	-0.18	0.09
H(5)	-0.01	-0.24	0.05

\*  $l_1, l_2, l_3$  are direction cosines with respect to  $a, b,$  and  $c^*$ , respectively;  $D$  is the distance of the plane from the origin.

† Bold-face type indicates that atom was used to define the plane. Positive deviations are in the direction of the origin.

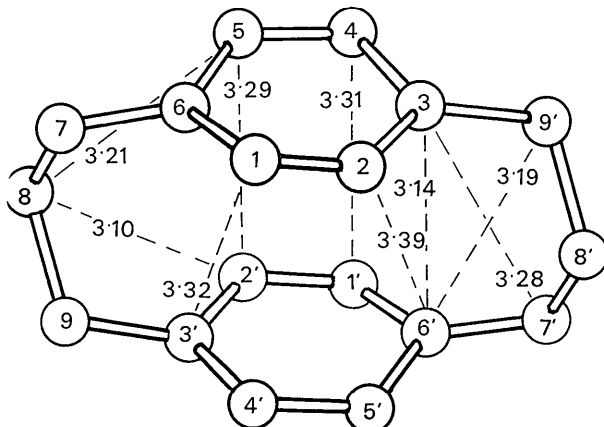


Fig. 5. Some non-bonded intramolecular contacts. See also Table 9.

(axis  $B$ ) and away from the molecular center, perhaps as a result of the contacts with C(8). These displacements are only on the borderline of significance and the similar apparent displacements of H(2) and H(5) in the same direction (Table 10) are not significant, since they are appreciably less than the e.s.d. in the position of a hydrogen atom, about 0.03–0.04 Å.

The geometry of the aromatic ring suggests that its distortion can be discussed in terms of a combination of two effects, a folding about the C(3)–C(6) axis, which would decrease the internal angles at C(3) and C(6) while preserving the other two angles at these atoms and also those at the other atoms of the ring, and a stretching along the C(3)–C(6) line, which would leave the ring planar, decrease the internal angles at C(3) and C(6), and increase the other internal angles in the ring and the external angles at C(3) and C(6). Most of the distortion in the aromatic rings of the diolefin of [2.2]paracyclophane (Coulter & Trueblood, 1963) could be discussed in terms of the folding alone, because most of the angles mentioned are about 120° except for the internal angles at the substituted atoms which are smaller by an average of 2.6°. The angle of fold, *i.e.* the dihedral angle between the two half-aromatic rings, is 16.4° in the diolefin, but is only 8° in the present molecule. The greater decrease in the internal angles at the substituted atoms in the [3.3] compound (average 3.2°) in spite of the smaller degree of folding is compensated for by increases in the other internal angles in the ring and in the external angles at C(3) and C(6) (Fig. 2 and Table 8).

The aromatic hydrogen atoms are displaced slightly, toward the inside of the molecule, from the plane of the half-aromatic ring to which they are attached (planes II and III of Table 10). The average displacement is about 0.08 Å and seems just significant. This effect is even more striking in the diolefin of [2.2] paracyclophane (Coulter & Trueblood, 1963, Fig. 5) and is observed also in [2.2] paracyclophane itself (Lonsdale, Milledge & Rao, 1960, Fig. 3; Bekoe & Trueblood, 1964). Cram has suggested to us that this is due to repulsion between  $\pi$ -electrons and C–H bonding electrons, the  $\pi$ -electron density being enhanced on the outside of the molecule because of inter-ring repulsion. Haigh (1963) has pointed out that the positions of these hydrogen atoms below the plane may be in part a consequence of torsion about the ring C–C bonds to C(3) and C(6); this explanation is in accord with the observation that the displacement is greater in the [2.2]-diolefin than in the present molecule, since the deformation angle  $\alpha$  is appreciably larger in that molecule.

The average aromatic bond distance of  $1.389 \pm 0.003$  Å in the present molecule is somewhat shorter than the value of  $1.397 \pm 0.001$  found for gaseous benzene by Raman spectroscopy (Stoicheff, 1954) and electron diffraction (Almenningen, Bastiansen & Fernholt, 1958; Kimura & Kubo, 1960) but does not differ significantly from that found for crystalline benzene by X-ray diffraction ( $1.392 \pm 0.004$ ) by Cox, Cruickshank



& Smith (1958). The above estimate of 0.003 Å as the e.s.d. of the average aromatic bond distance was arrived at by combining the effects of the uncertainties in the lattice parameters (estimated as 0.1%) and in the librational correction (arbitrarily estimated as 0.002 Å) with the e.s.d. of an average distance calculated by standard methods (Cruickshank & Robertson, 1953),  $0.003/\sqrt{6}$ . Although the error in the librational correction itself may be overestimated, there may of course be unknown systematic errors; thus it is questionable whether the difference between the present average aromatic bond distance and that in gaseous benzene is significant. The average of the C(1)–C(2) and C(4)–C(5) distances is not significantly different from the average of the other four aromatic distances.

The average distance between tetrahedral carbon atoms (1.531 Å) is in good agreement with Bartell's (1959) single bond distance of 1.533. Similarly, the average distance between tetrahedral and trigonal carbon atoms, 1.512 Å, does not differ significantly from the value  $1.505 \pm 0.003$  for isobutene (Bartell & Bonham, 1960) or from that of  $1.51 \pm 0.02$  for toluene (Keidel & Bauer, 1956). For propene, Lide & Christensen (1961) have reported the CH–CH<sub>3</sub> distance to be  $1.501 \pm 0.004$  Å.

The average C–H distance of  $0.98 \pm 0.02$  Å is significantly shorter than the normal C–H bond distance of 1.09 Å (*Tables of Interatomic Distances*, 1958). The distance is the same as that found in the diolefin of the [2.2] compound, and similar apparent shortenings have been noted many times before in X-ray studies. Tomiie (1958) has estimated an apparent shortening of C–H bonds of 0.1–0.2 Å because of shifts in electron density toward the carbon atom, the extent varying with apparent thermal motion. On the other hand, Cochran (1956) has estimated that, in benzene at least, the effect should be much smaller, only about 0.03 Å. This apparent shortening has been discussed recently by Jensen (1962) and Hamilton (1962), who attribute it to systematic errors either in the data or in the analysis thereof.

The molecule of [3.3]-*p*-cyclophane is considerably less distorted than the corresponding [2.2] compound or the [2.2] diolefin, and the strain energy is estimated to be only about 20 to 25% as great as in these other molecules (Table 11). The methods used in estimation of the strain energies are summarized in the Appendix. It is noteworthy that in each molecule most of the strain energy is due to the out-of-plane distortion of the aromatic system and its attached substituent atoms.

It is instructive to compare the distribution of strain in the [2.2] compound and its diolefin; we shall use the nomenclature of Coulter & Trueblood (1963) in designating the three unique angles in the side-profile of the molecules (Table 12). It is necessarily true that  $\delta - (\alpha + \beta) = 90^\circ$ ; furthermore it is obvious that the larger each of these angles becomes, the less the inter-ring repulsions (although if the angles become too large, the bridge atoms may move toward the center

Table 11. *Estimated contributions to strain energies of some paracyclophanes*<sup>(a)</sup>

	Diolefin of [2.2]	[2.2] <sup>(d)</sup>	[3.3]
Out-of-plane distortion of aromatic rings and <i>p</i> -substituents <sup>(b)</sup>	35	26	5
Abnormal non-bonded C–C repulsions <sup>(c)</sup>	2	2	–
In-plane deformation of ring angles	1	1	1
Bending at bridge atoms	1	0	1
Bond stretching	0	0 <sup>(d)</sup>	0
Eclipsing strain <sup>(e)</sup>	–	4	0
Total	39	33 <sup>(f)</sup>	7

(a) kcal.mole<sup>-1</sup>.

(b) Using Whiffen's (1955) potential function. Values are about 10% smaller if Coulson–Senent (1955) potential is used (see Appendix).

(c) That is, those differing significantly from those in unstrained model compounds.

(d) Calculations here for Brown's (1953a) model; there is no significant difference for that of Bekoe & Trueblood (1964). With the model of Lonsdale, Milledge & Rao (1960), the total is similar; the out-of-plane term is only about 23 kcal.mole<sup>-1</sup> but bond stretching adds about 7 kcal.mole<sup>-1</sup>.

(e) Estimated at 2 kcal for each pair of eclipsed methylene groups.

(f) These calculations were made in 1962; we have just learned of the precise calorimetric measurements by Boyd (1964) which give the value 31.3 kcal.mole<sup>-1</sup> for the strain energy in [2.2]-*p*-cyclophane. The agreement is appreciably better than the precision of our calculations.

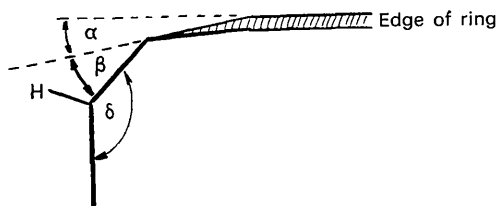
of the molecule so far that they approach some of the ring atoms too closely). Table 12 gives the hypothetical unstrained reference angles for a non-cyclic system (line 1), the values of the angles when the angle strain is minimized and inter-ring repulsion is ignored (line 2; see Appendix) and the angles in the actual molecules (line 3). The distortion in  $(\alpha + \beta)$  in the actual molecules is about 50% greater than that calculated when inter-ring repulsion is ignored, and in each case this increase in  $(\alpha + \beta)$  just about compensates the decrease in  $\delta$  between lines (1) and (2), so that in fact there is little strain in the angle  $\delta$ . However, because the normal value of  $\delta$  is 10° larger for the diolefin than for its saturated analog,  $(\alpha + \beta)$  is also larger in the diolefin and the total amount of strain is greater as a consequence. On the other hand, this increase in the out-of-plane distortion just about compensates for the smaller length of the bridge bond in the diolefin, and in fact the non-bonded inter-ring distances are comparable in the two molecules.

The increased flexibility in the three-carbon bridge of the [3.3] compound makes analysis of the distortion in this molecule more complex. With more rigid systems, Kitaigorodskii (1960) has successfully predicted conformations with the help of an averaged empirical potential which takes into account only bond-angle deformations and non-bonded repulsions, explicitly including 1,3-interactions. Hirshfeld (1963), Coulson & Haigh (1963), and others have recently made extensive calculations on deformations in overcrowded aromatic systems. As indicated in Table 11, most of the

Table 12. *Some deformation angles in the [2.2]-p-cyclophanes\**

[2.2]-p-Cyclophane		$\alpha$	$\beta$	$\delta$
[2.2]-p-Cyclophane	(1) Unstrained reference angles	0°	0°	112.5°
	(2) After minimizing angle strain with constraint	5.5	8	103.5
	(3) Actual molecule			
	(a) Brown, 1953a	11	14	115
	(b) Lonsdale <i>et al.</i> , 1960	14	7	111
	(c) Bekoe & Trueblood, 1964	13	10	113
Diolefin of [2.2]-p-cyclophane	(1) Unstrained reference angles	0	0	122.5
	(2) After minimizing angle strain with constraint	8	12	110
	(3) Actual molecule	14	15	119

\* Angles are defined by:



strain energy in the present molecule arises from out-of-plane distortions, with small contributions from bond-angle deformations. Since the dihedral angles in the side-chain are nearly normal, there is no significant contribution from 'eclipsing strain', which is appreciable in the analogous [2.2] compound. The inter-ring non-bonded distances are sufficiently great that the strain arising from this cause is negligible. Although in principle it should be possible to calculate the equilibrium conformation of the molecule given suitable potential functions for the different sorts of interactions which can occur, we have not been able to do this because of uncertainties about these potential functions and because of the relatively large number of degrees of freedom in the molecule.

We are indebted to the U.S. Air Force Office of Scientific Research for their support, to the staffs of the Western Data Processing Center and the U.C.L.A. Computing Facility for their cooperation in our use of the IBM 709 and 7090, and to Maryellin Reinecke, who prepared the illustrations.

## APPENDIX

Whiffen (1955) and Coulson & Senent (1955) have given potential functions from which the out-of-plane deformation energy of the aromatic system may be calculated. In the present molecules the distortion to be considered is a symmetrical boat-distortion, with the *para* ring-atoms displaced from the initial plane by  $Z$  and the attached substituent atoms displaced from the initial plane by  $z$ . As discussed in more detail elsewhere (Gantzel, 1962), Whiffen's eight-term quadratic valence-bond potential function leads to the following approximate expression for the deformation energy of each aromatic ring in a typical paracyclophane:

$$V = 3.48Z^2 - 1.46zZ + 0.30z^2 \quad (1)$$

(The units are  $10^{-11}$  ergs, with displacements in Å). In arriving at this expression, the distance to the exocyclic carbon atoms was taken as 1.51 Å (rather than the 1.05 assumed for C-H bonds by Whiffen); this implies the assumption of an equal restoring force for exocyclic carbon and hydrogen at the aromatic carbon atom. For small angular deviations,  $V$  may be expressed in terms of the angles  $\alpha$  and  $\beta$  (in radians) by the substitutions  $Z = 0.70\alpha$  and  $z = 1.51\beta + 2.21\alpha$ , which leads to:

$$2V = 1.82\alpha^2 + 0.92\alpha\beta + 1.37\beta^2 \quad (2)$$

where  $2V$  is now the out-of-plane deformation energy of the two rings of the molecule. Calculations were also made with the potential function of Coulson & Senent (1955); the corresponding terms of the first line of Table 11 were 31, 23, and 5 kcal. mole $^{-1}$ .

The potential for deformation of a C-C-C valence angle such as  $\delta$  is about  $0.4(\Delta\delta)^2$  (Pitzer & Donath, 1959), and since there are four such angles per molecule,  $1.6(\Delta\delta)^2$  should be added to (2) to include the strain in the angle  $\delta$ . The values of  $\alpha$ ,  $\beta$ , and  $\delta$  which minimize the energy subject to the constraint that  $\delta - (\alpha + \beta) = \pi/2$  may be calculated by adding a term  $t(\delta_0 + \Delta\delta - \alpha - \beta - \pi/2)$  and then setting the derivative with respect to each of the angular variables equal to zero (see, *e.g.*, Schomaker, 1951). ( $\delta_0$  is the reference or 'normal' value of  $\delta$ , and  $t$  is a so-called 'undetermined multiplier'). Of course in such a calculation, inter-ring repulsions are ignored, and so the resulting angles will not be realistic if these effects are significant.

The non-bonded C-C repulsions of Table 11 were calculated in terms of a Lennard-Jones 6-12 potential, with parameters suggested by Bartell (1960),  $2080/r^{12} - 2.26/r^6$  (again the units are  $10^{-11}$  ergs per molecule for  $r$  in Å).

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## The Structure of Nb<sub>6</sub>Sn<sub>5</sub>\*

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(Received 18 May 1964 and in revised form 3 August 1964)

The crystal structure of the intermetallic compound Nb<sub>6</sub>Sn<sub>5</sub> has been determined. The space-group symmetry was found to be *Immm* ( $D_{2h}^{22}$ ), and lattice parameters were measured as  $a = 5.656 \pm 0.002$ ,  $b = 9.199 \pm 0.003$ ,  $c = 16.843 \pm 0.004$  Å. The compound shows pronounced layering normal to the short axis.

### Introduction

Interest in niobium-tin alloys stems from the discovery of the structure and superconducting behavior of Nb<sub>3</sub>Sn (Matthias, Geballe, Geller & Corenzwit, 1954; Geller, Matthias & Goldstein, 1955). A number of

studies of the phase relationships in the system have been made (Agafonova, Baron & Savitskii, 1959; Wyman, Cuthill, Moore, Park & Yakowitz, 1962; Reed, Gatos, Lafleur & Roddy, 1962; Ellis & Wilhelm, 1964; Enstrom, Pearsall & Wulff, 1964; Schadler & Rosenbaum, 1964). Even though there is significant disagreement among the various proposed phase diagrams, nonetheless there is, with the single exception of the work of Agafonova, Baron & Savitskii, general agreement that two compounds exist on the tin-rich side of Nb<sub>3</sub>Sn. Both of these compounds have been reported to be superconducting; Reed & Gatos (1962) found a critical temperature of 16.6°K for 'Nb<sub>3</sub>Sn<sub>2</sub>' while van

\* Contribution No. 1522. Work was performed in the Ames Laboratory of the U.S. Atomic Energy Commission.

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