

THE CRYSTAL STRUCTURE OF A HEMI-DEWAR-NAPHTHALENE

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Dewar benzenes have been subjected to detailed structural analysis using electron diffraction,¹ microwave spectroscopy,² Raman spectroscopy,³ photoelectron spectroscopy,⁴ and theoretical calculation.⁵ The only X-ray analysis of a Dewar benzene has been performed on a chromium tetracarbonyl complex.⁶ We wish to report our results of the first direct determination of the X-ray structure of a Dewar molecule, using 1,3,6,8-tetra-*t*-butyl Hemi-Dewar naphthalene previously synthesized in our laboratories.⁷ The crystals were triclinic with the dimensions $a=6.301$ (1), $b=9.934$ (2), $c=19.995$ (4) Å, $\alpha=98.17$ (2), $\beta=95.49$ (2), $\gamma=105.34$ (2)^o. The unit cell contains two molecules and, as a result of the X-ray analysis, the space group was established as $P\bar{1}$. Three dimensional X-ray diffraction data was collected on two crystals using an Enraf-Nonius CAD-4 diffractometer with CuK α radiation. A slow decomposition of the crystal limited the quality of the data obtained; 3045 reflections were measured significantly above background. The orientation of the major part of the molecule was found both by direct phasing⁸ and from the Patterson map, but difficulty was experienced in finding the relative translation of the two molecules. A fragment of one molecule was therefore placed at an arbitrary position in the space group $P1$ and atoms added in from successive electron density maps until the second molecule appeared related by a center of symmetry to the first. Coordinates were transformed to the symmetry center as origin and a least squares refinement⁹ carried out in the space group $P\bar{1}$. Using anisotropic temperature factors, an R of 0.093 was obtained. Thirty six of the forty hydrogens were located from a difference electron density map. The positions of the remaining four, bonded to carbon atoms with high thermal parameters, were calculated using the program CALCAT.¹⁰ After adding the hydrogens (keeping their positional and thermal parameters fixed and refining anisotropically on the non-hydrogen atoms), a final R of 0.068 was obtained. The observed bond distances and angles are shown in the Figure. We note the C-1,4 bridge bond length of 1.591 Å agrees well with data of other experiments (Table 1). The very long C-1,10 bond of the cyclobutene (of 1.52 Å in HMDB)¹ is due to repulsion between *t*-butyls. The closest intermolecular contact observed in our crystal is 3.986 (7) Å between C₂₁ and C₂₁'. This value, within 3 esd, agrees well with twice the van der Waals radius for CH₃ which

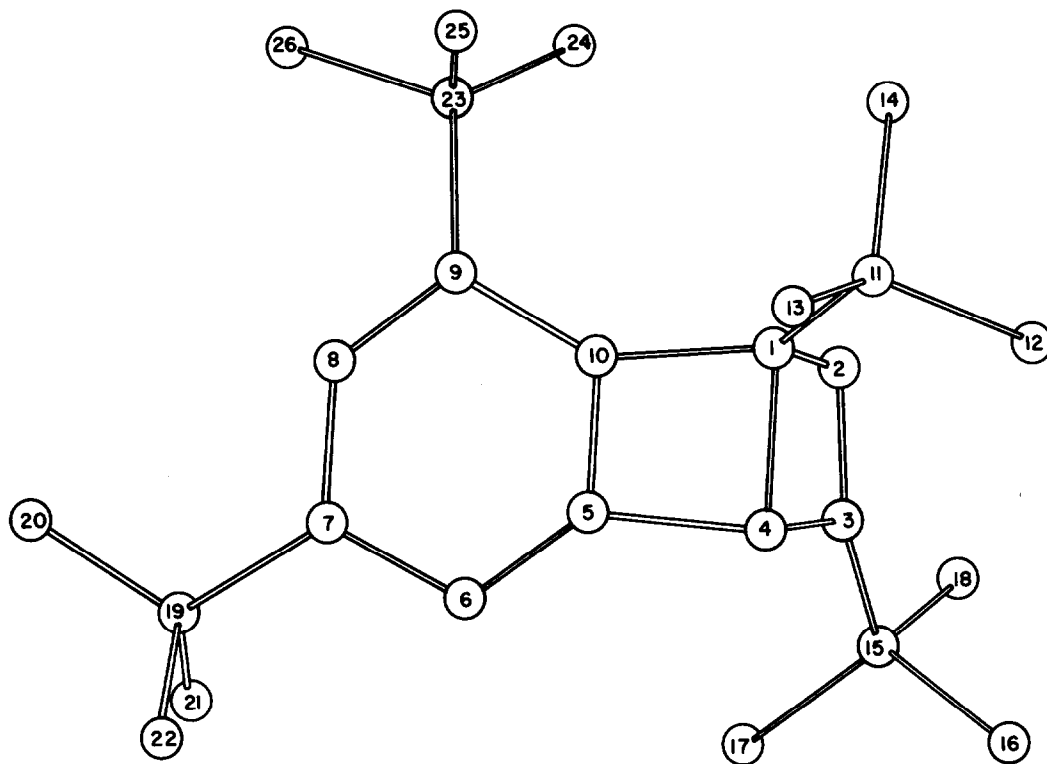


FIGURE 1

View of the Molecule Along the Direction Normal to the Mean Plane of
Atoms C1, C4, C5, and C10.

TABLE I

Bridge (1,4) bond length in Å and flap angle in degrees.

<u>Length Å</u>	<u>Flap°</u>	<u>Reference</u>
1.59	114	this work
1.63	124	hexamethyl dewar 1a
1.60	124	" 3
1.60	115,122	hexafluoro dewar 1b,1c
1.62	117	parent dewar 2
1.58	120	" " 4a
1.58	117	" " 5

is 2 \AA .¹¹ Thus, an evaluation of intramolecular crowding between peri-t-butyls reveals that the C-14, 24 distance is 3.570 (4) \AA while C-14, 25 is 3.744 (5) . The van der Waals strain from these two interactions is greatly reduced from that of the parent tetra-t-butyl naphthalene where there are 3 severe interactions.¹² The flap angle of the Dewar ring of 113.8° is the most acute angle reported (Table 1). There is also a second flap due to non-coplanarity of the benzene and the cyclobutene fused to it, presumably a result of the minimization of t-butyl repulsions. This is in contrast to the coplanarity revealed in an analysis of a simple benzocyclobutene.¹³ In our case the two mean planes make a flap of 174.6° in the same direction as the Dewar flap. This is of opposite sign to the 16° deviation (on 164° flap) from planarity of the vinyl methyl groups in hexamethyl Dewar benzene¹ which is zig-zag or *anti* whereas our Dewar naphthalene is *syn*. The benzene ring has large angle deviations similar to those of 1,2,4,5-tetra-t-butylbenzene.¹⁴ This last phenomenon, along with the decreased flap angle of the Dewar ring, the non-planarity of the benzocyclobutene moiety and the general phenomenon of bond-lengthening are necessary in order to prevent van der Waals repulsions greater than the ones observed.

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B O N D D I S T A N C E S

CARBON ATOMS	DISTANCE	CARBON ATOMS	DISTANCE
1-2	1.528 (4)	5-6	1.368 (3)
1-4	1.591 (3)	5-10	1.386 (3)
1-10	1.575 (3)	6-7	1.405 (3)
1-11	1.540 (3)	7-8	1.393 (4)
2-3	1.334 (4)	7-19	1.532 (4)
3-4	1.529 (4)	8-9	1.403 (4)
3-15	1.497 (4)	9-10	1.401 (3)
4-5	1.521 (3)	9-23	1.527 (4)

B O N D A N G L E S

CARBON ATOMS	ANGLES	CARBON ATOMS	ANGLES
2-1-4	84.7 (2)	6-5-10	125.8 (2)
1-2-3	95.4 (2)	5-6-7	116.6 (2)
2-3-4	94.2 (2)	6-7-8	118.2 (2)
1-4-3	85.6 (2)	7-8-9	125.8 (2)
4-1-10	85.5 (2)	8-9-10	113.9 (2)
1-4-5	86.9 (2)	5-10-9	120.6 (2)
4-5-10	95.3 (2)	10-9-23	125.0 (2)
1-10-5	92.3 (2)		