On the Structures of Strained Ring Systems. 3. Crystal and Molecular Structure of Naphtho[*b,e*]dicyclobutene

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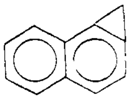
Abstract: The title compound crystallizes in the triclinic system, space group $P\bar{1}$, with cell constants of $a = 5.700$ (1) Å, $b = 6.790$ (3) Å, $c = 6.946$ (4) Å, $\alpha = 68.10$ (4)°, $\beta = 72.40$ (2)°, $\gamma = 86.87$ (3)°, $V = 237.24$ Å^3, mol wt 180.25 g mol^{-1}, d(calcd) = 1.261 g cm^{-3}, for $z = 1$ molecule in the unit cell. A data set was collected using Mo Kα ($\lambda = 0.71073$ Å) over the range of 6.0 to 60.0° in 2θ, which resulted in 1486 unique reflections, of which 748 had intensities above $3\sigma(I)$ and, thus, considered observed. The carbon skeleton of the molecule is completely planar (maximum deviation of any carbon atom from the least-squares plane is 0.013 (8) Å). Annelation of naphthalene by two cyclobutene rings causes small deviations in bond lengths from those of naphthalene, the largest of which is that associated with the 9, 10 C-C bond; the differences between the others are, by and large, negligible. The cyclobutene rings show a longer C-C bond at the annelated bond than those found in similar rings in annelated benzenes which, in turn, cause the internal angles at the points of fusion to be smaller than those in benzene derivatives. The observed C-C distance for the shared bond at the cyclobutene rings is 1.406 (3) Å, which is considerably longer than the value of 1.33 Å observed in the gas phase electron diffraction study of cyclobutene.

Introduction

The title compound was synthesized by Thummel and Natakul[2] who supplied us with *the* crystal used in this study. As pointed out by them, a series of homologues (I-VII) have been prepared by them and others[3-9] which offer the possibility of studying the effect of ring strain on the localization of electrons in the aromatic systems in question. We have already reported[1] that in the cases of two phenyl derivatives (IX and X) the structural parameters obtained in single-crystal, X-ray studies show no evidence of electron localization, despite several theories to the contrary.[10,11] It was our intention to determine whether the naphthalene system is more susceptible to showing the effects of strain caused by fused small rings as manifested by small, but observable, changes in structural parameters when compared with those of the parent molecule.[12] Compounds III and IV have already been studied crystallographically (for III, see ref 13; for IV, see ref 14), while naphthalene (XI) has been the subject of an intensive analysis, a final summary of which has been given by Cruikshank and Sparks.[12] Our results and comparisons with those obtained for III, IV, and XI are given below.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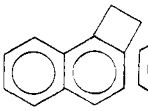
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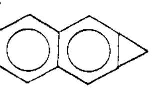
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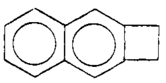
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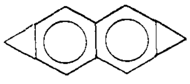
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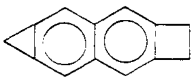
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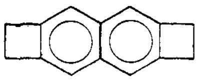
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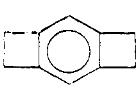
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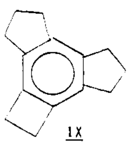
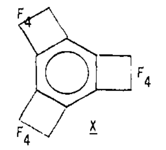

IX



X

Experimental Section

The crystal obtained from Dr. Thummel was a thin plate of approximate dimensions 0.93 × 0.65 × 0.08 mm. No effort was made to index the faces since the absorption coefficient (see Table I) is only 0.36 cm^{-1} for Mo Kα radiation, used throughout this study. The cell constants listed in Table I were obtained from the least-squares fitting of 49 reflections centered automatically on an Enraf-Nonius CAD-4 diffractometer. Refinement of the cell constants was carried out using the X-RAY '72 system of Stewart.[15] Data collection was carried out using procedures described in detail previously,[1] with those aspects of data collection and processing unique to this study summarized in Table I. The density was not measured since we had only one crystal which was used for further physical measurements by Dr. Thummel after we collected our X-ray information. However, given the nature of the refinement (see Table I) and the fact that the difference map calculated at the end of refinement had only low level, random noise, we feel that the content of the unit cell used in refinement is accurate and complete.

Our data decollation and reduction programs were written locally[16] and corrections for Lorentz and polarization effects, including the

Table I. Summary of Data Collection and Processing Parameters

space group	$P\bar{1}$
cell constants	$a = 5.700$ (1) Å $b = 6.790$ (3) Å $c = 6.946$ (4) Å $\alpha = 68.10$ (4)° $\beta = 72.40$ (2)° $\gamma = 86.87$ (3)°
cell volume	237.24 Å^3
molecular formula	$C_{14}H_{12}$
molecular weight	180.25 g mol^{-1}
density (calculated)[a]	1.261 g cm^{-3}
absorption coefficient	$\mu = 0.36$ cm^{-1}
radiation used (Mo Kα) (graphite crystal)	$\lambda = 0.71073$ Å
standards for intensity control (every 30)	[1,1,2; −3,1,1]
Bragg angle limits for data collection	$6.0° \leq 2\theta \leq 60.0°$
scan width for each reflection	$\Delta\theta = 1.20 + 0.35 \tan\theta$
maximum time for any scan	$t = 300$ s
range of scan speeds	0.37–3.35°/min.
minimum counts above background accumulated	1500
total number of data collected	1486
number of data above $3\sigma(I)$ used in refinement	748
total number of variables	88
final $R(F)$	0.046
final $R_w(F)$	0.041
weighting scheme	$w = 1/[\sigma(F)]^2$

[a] Only one crystal was available, which was used for data collection; density calculated for $z = 1$ molecule/unit cell.

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Table II. Positional and Thermal Parameters. Coordinates Were Multiplied by (Carbon Atoms × 10^4, Hydrogens × 10^3) Thermal Parameters (Carbon and Hydrogen Atoms × 10^3)

atom	*x/a*	*y/b*	*z/c*	U_{11} or U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	−1269 (4)	−0342 (4)	0628 (4)	32 (1)	35 (1)	35 (2)	−17 (1)	−10 (1)	1 (1)
C(2)	−2480 (5)	0432 (4)	2318 (4)	33 (2)	43 (2)	39 (2)	−19 (1)	−07 (1)	0 (1)
C(3)	−1149 (5)	1790 (4)	2671 (4)	43 (2)	38 (2)	37 (2)	−20 (1)	−12 (1)	6 (1)
C(4)	−1223 (6)	3104 (5)	4077 (5)	61 (2)	47 (2)	47 (2)	−27 (2)	−18 (2)	8 (2)
C(5)	1525 (6)	3880 (5)	2665 (5)	61 (2)	43 (2)	54 (2)	−25 (2)	−25 (2)	1 (2)
C(6)	1321 (5)	2465 (4)	1433 (4)	43 (2)	36 (2)	45 (2)	−20 (1)	−18 (1)	0 (1)
C(7)	2569 (5)	1792 (4)	−0194 (5)	35 (2)	41 (2)	42 (2)	−18 (1)	−10 (1)	−3 (1)
H(2)	−423 (4)	−009 (4)	319 (4)	47 (8)					
H(4A)	−148 (4)	224 (4)	566 (4)	42 (8)					
H(4B)	−242 (5)	428 (4)	389 (4)	71 (9)					
H(5A)	280 (5)	352 (4)	347 (4)	60 (9)					
H(5B)	176 (4)	539 (4)	172 (4)	51 (8)					
H(7)	426 (5)	234 (4)	−118 (4)	53 (8)					

Table III. Distances (Ångstroms) and Angles (Degrees) with Estimated Standard Deviations in Parentheses

A. Distances

C(1)-C(2)	1.436 (3)	C(6)-C(7)	1.363 (3)
C(1)-C(1)′	1.441 (4)	C(4)-H(4A)	1.01 (2)
C(2)-C(3)	1.358 (3)	C(4)-H(4B)	1.02 (3)
C(3)-C(4)	1.540 (3)	C(5)-H(5A)	1.01 (3)
C(3)-C(6)	1.406 (3)	C(5)-H(5B)	0.98 (2)
C(4)-C(5)	1.571 (4)	C(7)-H(7)	0.99 (2)
C(5)-C(6)	1.534 (3)	C(2)-H(2)	1.00 (2)
C(1)′-C(7)	1.430 (3)		

B. Angles

C(1′)-C(1)-C(7′)	120.0 (3)	H(4A)-C(4)-H(4B)	110.8 (20)
C(1′)-C(1)-C(2)	119.7 (3)	C(4)-C(5)-C(6)	87.1 (2)
C(2)-C(1)-C(7′)	120.2 (2)	C(4)-C(5)-H(5A)	116.5 (15)
C(1)-C(2)-C(3)	117.7 (2)	C(6)-C(5)-H(5A)	116.6 (14)
C(1)-C(2)-H(2)	118.2 (12)	C(4)-C(5)-H(5B)	114.1 (15)
C(3)-C(2)-H(2)	124.1 (12)	C(6)-C(5)-H(5B)	111.7 (14)
C(2)-C(3)-C(4)	144.5 (2)	H(5A)-C(5)-H(5B)	109.5 (20)
C(2)-C(3)-C(6)	122.4 (2)	C(3)-C(6)-C(5)	93.1 (2)
C(4)-C(3)-C(6)	93.0 (2)	C(3)-C(6)-C(7)	122.6 (2)
C(3)-C(4)-C(5)	86.8 (2)	C(5)-C(6)-C(7)	144.2 (2)
C(3)-C(4)-H(4A)	114.8 (13)	C(6)-C(7)-C(1′)	117.5 (2)
C(5)-C(4)-H(4A)	115.4 (13)	C(6)-C(7)-H(7)	124.4 (13)
C(3)-C(4)-H(4B)	113.4 (15)	C(1′)-C(7)-H(7)	117.9 (10)
C(5)-C(4)-H(4B)	113.9 (15)		

Table IV

A. Equation of the Least-Squares Plane through the Carbon Atoms in Orthogonal Ångstrom Space

$$0.4967x - 0.7772y + 0.3961z = -0.0024$$

B. Deviations from the Plane (Ångstroms)

C(1)	−0.001	C(5)	−0.011
C(2)	−0.008	C(6)	−0.002
C(4)	−0.000	C(7)	0.002
C(4)	0.013		

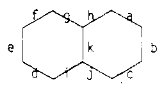
effect of partial polarization by the monochromator crystal (dense graphite; assumed to be ideally imperfect; see ref 17), were applied. The structure was solved from the reduced data set using Germain, Main, and Woolfson's program MULTAN,[18] from which the most probable solution gave all seven carbon atoms in the asymmetric unit. The molecule is positioned in the cell such that an inversion center is midway between C(1) and its symmetry relative, C(1′), giving 1/2 molecule/asymmetric unit. All subsequent data processing was carried out with Sheldrick's programs (the 1976 version of SHEL-X).[19] Hydrogen atoms were found in a difference map and refined isotropically to the values given in Table II, which lists the positional and anisotropic thermal parameters of the carbon atoms also. Refinement converged to the residuals $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.046$ and $R_w(F) = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2} = 0.041$ where w, the weights, are given by $w = [1/\sigma(F_o)]^2$ and the values of $\sigma(F_o)$ are calculated on the assumption that counting obeys Poisson statistics.

Bond lengths and angles are listed in Table III, with standard deviations calculated from the inverse matrix of the last cycle of refinement. A least-squares plane was calculated through all the carbon atoms and deviations of atoms from that plane were computed; the results are listed in Table IV. Finally, Table V gives a summary of our results and compares them with those of compounds III, IV, and XI (naphthalene). All drawings were generated using Johnson's ORTEP-2.[20] Figure 1 shows the molecule, together with the numbering system employed in the crystallographic study, while Figure 2 shows the packing of the molecules in the unit cell.

Description of the Structure and Discussion

The entire carbon skeleton of the molecule is planar (see Table IV and the stereofigures, Figures 1 and 2). The largest deviation of any atom from the plane is 0.013 (8) Å, which is negligible. These results are in agreement with those obtained for similarly annelated aromatic systems (III, IV, VIII-X) reported earlier,[1,13,14,21] as well as those results in somewhat related systems described by Davis and co-workers.[22] The aromatic hydrogens lie in the plane of the naphtho carbons with deviations $<3\sigma$ from that plane. Furthermore, the aliphatic and aromatic hydrogens have C-H distances ranging from 0.98

Table V. Bond Lengths (Ångstroms) in Naphtho[*b,e*]dicyclobutene and Related Molecules Containing a Naphthalene Nucleus



compd	bonds shown below correspond to above diagram[a]											ref
	a	b	c	d	e	f	g	h	i	j	k	
XI	1.364 (5)	1.415 (5)	= a	= a	= b	= a	1.421 (5)	= g	= g	= g	1.418 (5)	12
III[b]	1.337	1.368	= a	1.362	1.403	= d	1.408	1.437	= g	= h	1.439	13
IV[c]	1.354	1.407	1.354	1.361	1.404	1.360	1.416	1.423	1.417	1.422	1.432	14
VII	1.358 (3)	1.406 (3)	1.363 (3)	= a	= b	= c	1.430 (3)	1.436 (3)	= h	= g	1.441 (4)	this study

[a] In III and IV; the common bond with the annelated ring is b. [b] Located at a mirror plane; errors stated are in the range of 0.004-0.006 Å for the C-C bonds. [c] At a general position; errors in C-C distances were estimated to be 0.002 Å on the average.

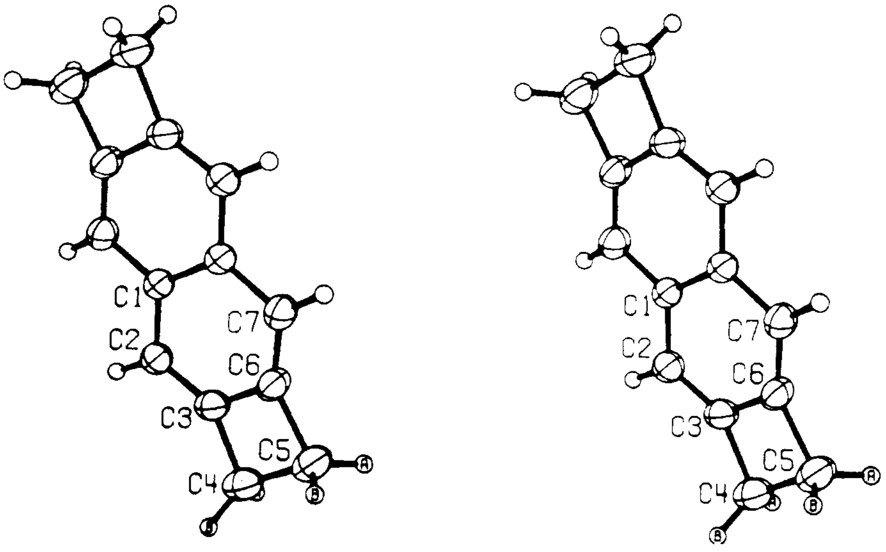


Figure 1. Stereoview of the molecule showing the numbering system used in the crystallographic study. The ellipsoids are 50% probability, except for the hydrogens whose size is arbitrarily chosen for representational convenience.

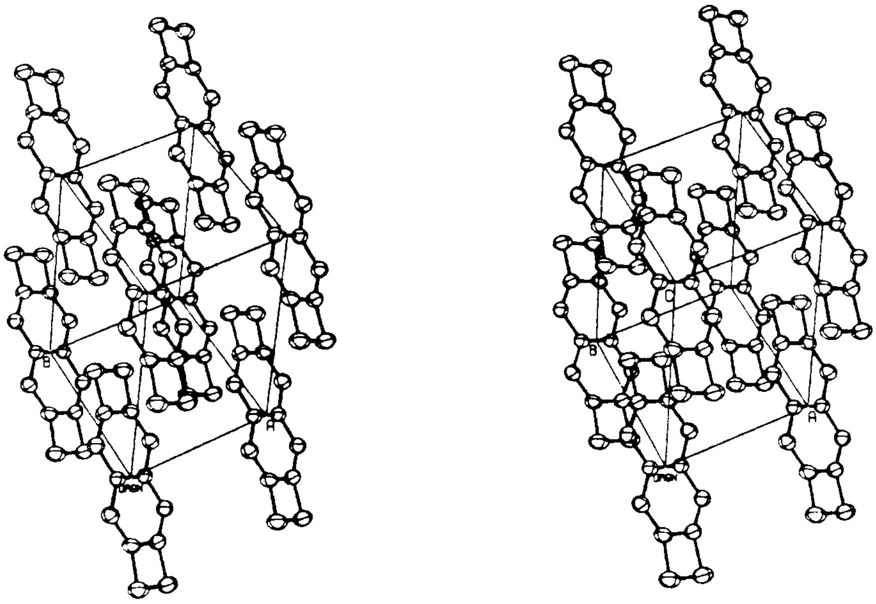


Figure 2. The packing of the molecules in the triclinic cell. The molecules are located on inversion centers at each vertex of the unit cell.

(2) to 1.02 (3) Å, which is one to two standard deviations from the accepted (neutron diffraction) value of 1.03 Å.

The most important part of the molecular description is, of course, the distribution of C–C distances of the naphtho ring and the possibility that the observed pattern in VII is meaningfully different from that in naphthalene (XI). For that purpose, we have prepared Table V which summarizes the values observed for XI in the detailed study of this molecule by Cruikshank and Sparks,[12] for III in the recent studies by Billups et al.,[13] for IV by Crawford and Marsh,[14] and for the current study of VII. There is a simple and interesting pattern for bonds a, b, and c, which are those associated with the strained portion of the molecule in III, IV, and VII collectively. The pattern is as follows. III, which has the largest strain due to the annelated three-membered ring, shows bonds a and c compressed from the value of 1.364 (5) Å in naphthalene to 1.337 (4–6) Å. The strain, being less in the four-membered annelated systems (IV and VII), produces smaller compressions to 1.354 (2) and 1.358 (3) Å, respectively. Note that the value found by Crawford and Marsh[14] is identical within stated standard deviations with our value for VII, with both significantly different from the measured value found in III.[13] These two positions (a and c) are those expected to have increased double-bond character due to efforts by the three-membered ring to relieve strain associated with having a double bond within the ring. Thus, the prediction that those two bonds exocyclic to the strained three-membered annelated rings should increase in double-bond order seems to be met in the example listed in Table V. Note that, in IV and VII, bonds a and c were measured independently and are, as expected by symmetry, virtually identical. The differences for these bonds with those of naphthalene (XI) are statistically insignificant, as was found in the case of five- and four-membered annelated rings in our previous studies of benzene derivatives,[1] as well as in the case of VIII, studied by Lawrence and MacDonald.[21] Note also that the values for bonds d and f agree well for XI and III since that portion of the latter contains no annelated ring; therefore, it is not surprising that the others agree as well, in view of the observations above on four-membered annelated ring compounds. With regard to bonds g, h, i, and j whether measured independently or related by symmetry to another bond, the results are internally consistent in all cases and can only be compared in pairs. That is, naphthalene (XI) and our compound (VII) fall into one class, having either no annelation or symmetrical annelation at both sides, while III and IV are fused at a single side of the naphthalene nucleus. Note that our measured values of g, h, i, and j are statistically identical, as would be expected for this molecule. In all four cases our measured values are somewhat larger $(\sim 3\sigma)$ than those found by Cruikshank and Sparks[14] for naphthalene, which would be predicted for a small increase in the double-bond order at bonds a, c, d, and f of our compound (VII). In all the annelated systems, bond k is larger than that observed in naphthalene.

Finally, excellent agreement is also found between the cyclobutene moiety of VII and the analogous portions of similar molecules.[1,14,21,22] The shared bond is invariably longer when the fusion is to a naphthalene group, as opposed to a benzene group. Since the saturated C–C bond lengths are essentially the same in all cases, this results in necessarily smaller internal angles adjacent to the points of fusion in the cyclobutene group for IV and VII. Slightly longer bonds C(3)–C(4) and C(5)–C(6) are noted in VII than in all the other studies, but the reason for this is not apparent. In all cases, the shared bond is considerably longer than the value of 1.33 Å determined by gas phase electron diffraction for the double bond of cyclobutene.[23]

No unusually short intermolecular contacts are noted in VII. The planarity of the molecule allows for close packing in the lattice, as can be seen in Figure 2, and may account for trends found in the melting point behavior of the substituted naphthalenes and benzenes.[2]

Acknowledgments. We thank the U.S. National Science Foundation for funds to purchase the diffractometer (Grant MPS-74-13718) and for operational support (Grant CHE-77-11856), the Robert A. Welch Foundation for a research grant (E-594), and the University of Houston Computer Center for the very generous supply of free computing time and other services.

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Liquid-Phase Reactions of Free Methyl Cations from the Decay of Methane-t_4. Alternative Alkylation Sites in Halobenzenes

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Abstract: The reaction of free methyl cations, generated from the decay of multitritiated methane dissolved in liquid halobenzenes, gives the corresponding labeled halotoluenes together with methyl halides, toluene, and minor amounts of decomposition products. The attack of the reagent on the n-type nucleophilic centers displays a remarkable selectivity, following the trend Br > Cl > F, in agreement with the HSAB principle. Ring alkylation is characterized by an appreciable positional selectivity, which is in contrast with the scarce substrate discrimination. The reactivity ratios deduced from the competition experiments depend on the composition of the system, the selectivity of the reagent increasing with the concentration of halobenzenes. This trend is explained by the intervention of methylphenylhalonium ions, which, besides being intermediates for the formation of methyl halides, are also methylating agents and are more selective than free methyl cations.

The reactivity of electrophilic carbon toward aromatic substrates has been the object of continued interest for many years. Depending upon the experimental conditions (the reagent, the medium, the catalyst etc.), a large variety of alkylating species were either postulated or identified as responsible for the attack on the aromatic substrate.[1] Terms such as polarized molecules, polarized complexes and ion pairs,[2] and incipient and "hot" carbonium ions[3] were coined to describe reagents where carbon electrophilicity is promoted by the use of poorly solvating media[4] and methods favoring the formation of charged species as free of external influence as possible in solution.

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