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THE CRYSTAL AND MOLECULAR STRUCTURE OF AN UNUSUAL CONJUGATED HYDROCARBON

CYCLOOCTA[1,2,3,4-*def*]BENZO[3,4]CYCLOBUTA[6,7]BIPHENYLENE[1]

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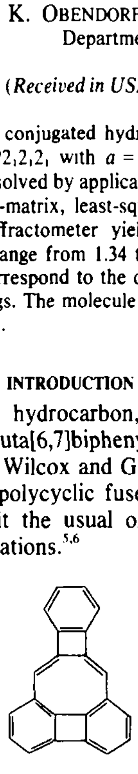
Abstract—The conjugated hydrocarbon, cyclo[1,2,3,4-*def*]benzo[3,4]cyclobuta[6,7]biphenylene, crystallizes in the space group $P2_12_12_1$ with $a = 15.136(4)$, $b = 16.453(4)$, $c = 5.584(1)$ Å, $Z = 4$, $\rho_{cal} = 1.32$, $\rho_{obs} = 1.31\ g\ cm^{-3}$. The structure was solved by application of direct methods after reducing the dominance of *hk*0 reflections in starting set selection. Full-matrix, least-squares refinement of 1910 independent data collected with MoK_α radiation on a four-circle diffractometer yielded a final conventional $R = 0.068$. Bond lengths in this unusual conjugated hydrocarbon range from 1.34 to 1.53 Å. Calculated iterated-Hückel bond lengths that include effects of σ strain reasonably correspond to the observed bond distances, with the largest differences (0.03 Å) occurring in the four membered rings. The molecule is essentially planar, but exhibits an overall bowing that is probably due to crystal packing forces.

INTRODUCTION

The conjugated hydrocarbon, cycloocta[1,2,3,4-*def*]benzo[3,4]cyclobuta[6,7]biphenylene (**1**) has recently been synthesized by Wilcox and Grantham[2] as part of a study of a class of polycyclic fused 4*n* systems[3,4] that does not formally fit the usual olefinic, aromatic and antiaromatic classifications.[5,6]



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The bond lengths for a number of such hydrocarbons have been predicted[7] using the SCF model of Lo and Whitehead[8] which is based on the theory of Pople[9] and of Pariser and Parr.[10] An X-ray diffraction study of **1** was undertaken to fully characterize the bonding pattern in this unusual molecule and to provide the basis for further refinement in bond length calculation.

EXPERIMENTAL

Orthorhombic crystals, space group $P2_12_12_1$, were obtained from a methanol and acetone solution of the compound. The cell dimensions are $a = 15.136(4)$, $b = 16.453(4)$, $c = 5.584(1)$ Å with $Z = 4$; the densities are $\rho_{obs} = 1.31$, $\rho_{cal} = 1.32\ g\,cm^{-3}$. The diffraction intensities of a $0.6 \times 0.15 \times 0.14$ mm crystal were measured on a Picker FACS-1 four-circle diffractometer in a θ-2θ scan mode with Zr filtered MoK_α radiation. Each scan included a variable increment in angle above the 1.7^c minimum to allow for spectral dispersion; background counts of 40 sec duration were taken at both limits of each scan. Reflections within one octant of reciprocal space out to $2\theta = 56.83°$ were collected. Of the 1910 independent reflections measured, 1808 were above the threshold value determined by the criterion $|F_o| \geq 1.58\sigma_F$. The observed structure factor (F_o) and its standard deviation (σ_F) are defined as $F_o = [(C - kB)/Lp]^{1/2}$ and $\sigma_F = (C + k^2B)^{1/2}/2F_oLp + 0.02\ F_o$, where C and B represent total scan counts and background counts respectively, k is the ratio of scan time to background count time, *Lp* is the Lorentz-polarization correction. Three standards were measured at intervals of 50 reflections to monitor alignment and possible deterioration of the crystal during the data collection period. No standard intensity varied more than 3% of the initial intensity during the collection of data.

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by direct methods with the program MULTAN.[11] As experienced with other fused ring structures,[12–14] the initial attempts to determine phases by application of direct methods failed to yield the structure. It was anticipated from previous analyses of the distribution of |E| values for similar structures[1,12] that special subsets of reflections with abnormally high |E| values can result in the selection of unsuccessful starting sets. Indeed, in the present case 13 of the 50 reflections with highest |E| values were of the class *hk*0 with high values of *h* or *k*. To eliminate the pseudo-periodicity thus introduced, 12 reflections of this class with $|E| \geq 2.05$ were removed from the selection process for the starting set. Except for the 11 17 0 reflection ($|E| = 3.70$) that was specified as an origin determining reflection, the program MULTAN was allowed to select a new starting set using 179 reflections with $|E| \geq 1.50$ in the phase determination. The E-Fourier synthesis of the resulting phases contained all 22 carbon atoms of the structure.

The atomic coordinates and anisotropic thermal parameters were refined by full-matrix, least-squares method[15] using a weighting function $w = 1/\sigma_F^2$. The quantity minimized in the least-squares calculation was $\Sigma w(|F_o| - |F_c|)^2$. The sources of atomic scattering factors were Cromer and Mann[16] for C and Stewart *et al.*[17] for H. The H atoms were located in calculated positions 0.95 Å from the bonding C atom in the plane of the hydrocarbon ring and assigned isotropic thermal parameters 0.5 Å^2 higher than that of the bonding C atom. The hydrogen positions and isotropic thermal parameters were included but held constant in the final cycles of least-squares refinement. A secondary extinction correction[18] was applied.

The final conventional residual for 1910 reflections was $R_1 = 0.068$, and the weighted residual $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$ was 0.066 with a data-to-parameter ratio of 9.5:1. Atomic coordinates for the carbon atoms are given in Table 1. A perspective

Table 1. Final atomic fractional coordinates for carbon atom[a] and deviations of atoms from planes through parts of the molecule (Å)

Atom	10^4 x/a	10^4 y/b	10^4 z/c	Δ_1[b]	Δ_2[c]
C(1)	4921(2)	5903(2)	-3301(6)	-0.025	0.004
C(2)	4375(2)	6094(2)	-5296(6)	-0.025	-0.029
C(3)	3642(2)	5639(2)	-5870(6)	0.031	-0.018
C(4)	3382(2)	4950(2)	-4562(6)	0.074	0.007
C(5)	3905(2)	4756(2)	-2649(6)	0.063	0.027
C(6)	4131(2)	4184(2)	-583(6)	0.029	0.002
C(7)	3930(2)	3512(2)	747(6)	0.042	0.001
C(8)	4521(2)	3344(2)	2637(7)	-0.012	-0.020
C(9)	5242(2)	3824(2)	3158(6)	-0.052	-0.014
C(10)	5445(2)	4534(2)	1792(6)	-0.046	0.008
C(11)	4874(2)	4672(2)	-38(6)	-0.015	0.005
C(12)	4656(2)	5233(2)	-2064(6)	0.016	0.026
C(13)	5696(2)	6392(2)	-2696(5)	-0.077	0.000
C(14)	6269(2)	6294(2)	-869(5)	-0.074	0.038
C(15)	6464(2)	5738(2)	1297(5)	-0.034	0.038
C(16)	6190(2)	5063(2)	2414(6)	-0.029	0.073
C(17)	7200(2)	6298(2)	1852(6)	-0.003	0.167
C(18)	7868(2)	6456(2)	3488(6)	0.082	0.296
C(19)	8373(2)	7146(2)	3033(7)	0.102	0.350
C(20)	8202(2)	7644(2)	1060(6)	0.052	0.291
C(21)	7536(2)	7481(2)	-565(6)	-0.036	0.160
C(22)	7038(2)	6790(2)	-108(6)	-0.062	0.099

[a] The estimated standard deviations in parentheses apply to the last significant digit.[19]

[b] Deviation of atoms from the least-squares plane through the entire molecule. The equation of this plane is:

$$0.59081x - 0.54818y - 0.59197z = 0.14216.$$

[c] Deviation of atoms from least-squares plane through the biphenylene group of molecule. The equation of this plane is:

$$0.56332x - 0.56294y - 0.60478z = -0.15335$$

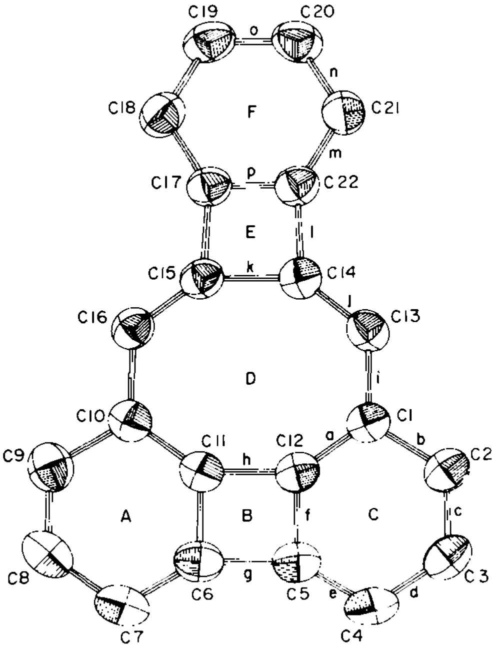

Fig. 1. A perspective view of the molecule.

illustration of the molecule is presented in Fig. 1. The calculated hydrogen positions, the anisotropic thermal parameters, and a Table of calculated and observed structure factors are available.†

RESULTS AND DISCUSSION

The bond lengths observed in this conjugated hydrocarbon (Table 2) range from 1.34 Å to 1.53 Å. A rigid-body least-squares analysis[20] of the anisotropic thermal parameters of the carbon atoms resulted in corrected bond lengths which were 0.001–0.002 Å longer than the uncorrected bond lengths. The observed bond lengths compare favorably with those predicted[7] using the Lo and Whitehead model[8] (Table 2). The pattern of alternating bond lengths predicted for **1** was observed. However, the bond distances that were predicted to be short were observed to be even 0.01–0.02 Å shorter than the calculated bond length. Similarly, the bond distances that were predicted to be long were from 0.01–0.07 Å longer than predicted. Similar disagreements between calculated and observed bond distances were observed in benzenoid structures by Lo and Whitehead.[8]

These discrepancies are not too surprising in the present case since the Lo-Whitehead SCF π-electron model is parameterized on conventional aromatic species and might not be able to accommodate the unusual sigma framework present in **1**. In order to explore this question, a series of model calculations was carried out. First, a Hückel calculation was performed using a variable β_{ij} program that iterates to self-consistent bond orders.[2] The standard deviation between the calculated and observed values was 0.022 Å (the standard deviation using the much more sophisticated SCF model was 0.019 Å). The largest discrepancies were associated with certain of the bonds of the 4-membered rings. Since it is known that such bonds are exceptionally long (by 0.03 Å in the case of cyclobutane[21]) it was suggestive that the *average* discrepancy of the calculated eight 4-membered ring bonds was about −0.03 Å. Simply incrementing these eight calculated bond lengths would not be appropriate since the deviations covered a range from +0.025 to −0.083. To determine if the remaining discrepancies in the model can

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†See NAPS document #02837 for 9 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, 440 Park Avenue South, New York, N.Y. 10016. Remit in advance $3.00 for microfiche copy or $5.00 for photocopy. All orders must be prepaid. Foreign orders add $3.00 for postage and handling.

Table 2. Interatomic distances (Å)

Bond	Observed Bond Distance[a]	Bond[b]	Observed Bond Distance[a]	Average Bond[c] Distance	SCF Bond Lengths	Iterated-Hückel Bond Lengths Including σ Strain
a	1.362(4)	a′	1.358(4)	1.360	1.394	1.371
b	1.422(4)	b′	1.428(4)	1.424	1.419	1.421
c	1.377(4)	c′	1.378(4)	1.378	1.387	1.392
d	1.404(5)	d′	1.410(5)	1.407	1.416	1.419
e	1.368(4)	e′	1.366(4)	1.367	1.389	1.374
f	1.418(4)	f′	1.416(4)	1.417	1.418	1.431
g	1.528(4)			1.528	1.484	1.505
h	1.497(4)			1.497	1.485	1.487
i	1.462(4)	i′	1.466(4)	1.464	1.469	1.450
j	1.349(4)	j′	1.340(4)	1.344	1.350	1.363
k	1.546(4)			1.546	1.478	1.523
l	1.483(4)	l′	1.479(4)	1.481	1.472	1.485
m	1.388(4)	m′	1.387(4)	1.388	1.403	1.386
n	1.382(4)	n′	1.391(4)	1.386	1.401	1.403
o	1.398(5)			1.398	1.401	1.404
p	1.384(4)			1.384	1.412	1.417

[a] The estimated standard deviations in parentheses apply to the last significant digit.[19]

[b] The primed bond distances are the observed distances for the equivalent bond in the other half of the molecule (Figure 1).

[c] Average of bond distances from both sides of molecule.

be associated with the strains introduced when the rings were combined, a second calculation was performed using an empirical force field energy minimization program.[22] The force field of Boyd was employed using the iterated-Hückel bond lengths as the unstrained values except that, at the outset, the 4-membered ring bonds were incremented by +0.03 Å. The C–C stretching constants were altered slightly to reflect the varied bond orders around the rings but this variation was not a major factor in the results. The output of the Boyd program provided a set of bond length distortions that minimized the sigma distortion energy. Another iterated-Hückel calculation was then carried out in which the bond lengths were biased by these calculated geometric distortions. In principle, one could repeat this cycle of calculations, first minimizing the π-energy and then the σ-energy, but the inherent limitations of the approximations in the models do not justify such a treatment. The several bond lengths referred to above are given in Table 2. By this treatment, the standard deviation between the observed and calculated lengths were reduced to 0.012 Å, which approaches the experimental uncertainty. The marked improvement in agreement supports the idea that the major source of disagreement was the inadequate treatment of the σ-framework in the π-electron model. There appears to be no need to invoke some special electronic effect arising from the presence of 4 n-membered rings other than that reflected in the simple one-electron (Hückel) or single determinant (SCF) models.

In the crystal, the molecule occupies a general position, thus losing the mirror symmetry inherent in the free molecule. Nevertheless, the largest difference in equivalent bond distances in the two halves of the molecule is within two standard deviations and the largest bond angle discrepancy is only 2°. The principal effect of the asymmetric site is a slight bowing of the molecule from a planar configuration; nevertheless the greatest deviation from the least-squares plane through the molecule is 0.10 Å for C(19) (Table 1). The magnitudes of the distortions are given by the dihedral angles between planes in the molecule (Table 3) and the deviation of atoms from the plane of the biphenylene group (Table 1); they are similar to those reported for related systems, *i.e.* triphenylene,[23] naphtho[b]cyclobutene[24] and biphenylene.[25]

The question arises as to whether the observed

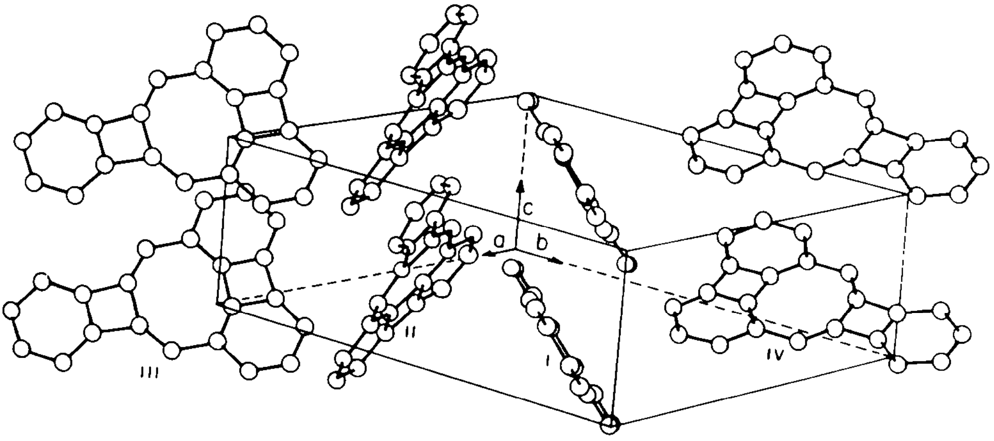

Fig. 2. Packing of molecules in the crystal. The equivalent positions of the molecules are: i: x, y, z; ii: ½ − x, −y, ½ + z; iii: ½ + x, ½ − y, −z; iv: −x, ½ + y, ½ − z.

Table 3. Dihedral angles

Planes[a,b]	Angle
i to ii	72.6°
i to iii	72.4
i to iv	66.5
A to B	0.3
A to C	1.0
B to C	1.3
B to D	1.7
B to F	5.8
ABC to D	1.1
ABC to F	5.3
C to D	1.1
C to F	5.2
D to E	2.5
E to F	1.9

[a] The molecules i, ii, iii, iv are as defined in Figure 2.

[b] The rings of the molecule, A through F, are as defined in Figure 1.

distortions can be accounted for by intermolecular interaction forces. The total distortion energy is quite small since it is well distributed over the entire molecule; if the simplified force field of Coulson and Senent[26] is employed, a total distortion energy of about 0.16 kcal/mole can be calculated. This value can be compared with the C–H interaction energy estimated from the van der Waals curve of Boyd[22] which gives an E_{CH} at 2.50 Å of 0.28 kcal/mole and a first derivative of −1.53 kcal/mole-Å. Since the maximum linear displacement from the mean plane of the biphenylene group is 0.35 Å, it can be seen that very modest intermolecular interactions would be sufficiently large to cause the observed distortion.

The packing coefficient of this crystal is 0.74 as defined by Kitaigorodsky.[27] A majority of organic crystals have packing coefficients in the range 0.65–0.77. The closest stacking of molecules in the crystal is between layers related through translation in the *c* direction of the crystal (Fig. 2). The distance between the parallel layers of molecules is 3.31 Å; the closest C-C distance in the stacked region of the biphenylene group is 3.37 Å.

The relationship between the 4 molecules in the unit cell illustrates molecule packing on the dovetail principle of organic chemical crystallography. A packing diagram of the molecules in the four equivalent positions in the unit cell is presented in Fig. 2, and the dihedral angles between the mean planes of the molecules are given in Table 3. Analogous stacking patterns have been observed in several non-linear aromatic molecules, *i.e.* coronene,[28] pyrene[29] and 1,12-benzperylene.[30]

SUMMARY

The pattern of alternating bond lengths observed for hydrocarbon **1** is in good general agreement with SCF calculations although the calculated bond distances in the four membered rings deviate as much as 0.05 Å from those observed. Including sigma strain in an interated-Hückel bond length calculation more accurately reproduces the bond lengths observed in the X-ray diffraction study (standard deviation 0.012 Å and maximum deviation 0.03 Å). The slight non-planarity of the molecule appears to be accountable for in terms of packing forces.

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