

The Molecular Structures of Thiele's and Chichibabin's Hydrocarbons

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Abstract: Low temperature (~ 160 °C), inert atmosphere X-ray crystal structures have been obtained for Thiele's (α, α' - α, α' -tetraphenyl-*p*-xylylene, 3,6-bis(diphenylmethylene)-1,4-cyclohexadiene) and Chichibabin's ($\alpha, \alpha, \alpha', \alpha'$ -tetraphenyl-di-*p*-xylylene, [1,1'-biphenyl]-4,4'-diylbis[diphenylmethyl]) hydrocarbons. The latter compound is extremely oxygen sensitive. The carbon-carbon distances of the basic skeleton of Thiele's hydrocarbon are only slightly different than those in *p*-xylylene, suggesting that the increased kinetic stability of Thiele's hydrocarbon relative to the parent is largely attributable to steric protection by the four phenyl substituents, which are rotated an average of 43° out of the plane. The phenyl groups in Chichibabin's hydrocarbon are twisted similarly. The most striking conformational feature, however, is the planarity of the di-*p*-xylylene nucleus. In addition, the carbon-carbon bond lengths in this segment of the molecule are highly abnormal, lying roughly halfway between double bond and single bond values. Several lines of evidence indicate that Chichibabin's hydrocarbon has a singlet ground state with an unusually large amount of diradical character. Crystals of Chichibabin's hydrocarbon are bright green and have a pronounced metallic luster. The crystal packing is discussed briefly.

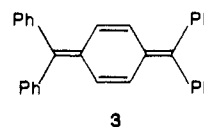
p-Xylylene¹ (**1**), an unsaturated hydrocarbon of theoretical² and commercial³ interest, polymerizes rapidly in the condensed phase at room temperature.^{4,3a} Considerable effort has been expended in ascertaining the multiplicity of *p*-xylylene's ground state. Much of the chemistry of this compound, such as its facile polymerization to poly-*p*-xylylene, is readily visualized in terms of a diradical **2**.^{4,3a,5} In spite of this general pattern of reactivity,



electron spin resonance (ESR),^{5,6} proton magnetic resonance,⁶ ultraviolet,⁷ infrared,^{7b} and photoelectron spectroscopic⁸ studies

unanimously concur that *p*-xylylene's lowest electronic state is a singlet. Ab initio and semiempirical molecular orbital (MO) calculations support this assignment.² Moreover, several authors have pointed out that there is a modest diradical component to the molecular wave function.^{2g,i,8} This does not appear to be the source of the high reactivity of *p*-xylylene, which has been ascribed to kinetic instability rather than ground-state destabilization.^{2j} A high-temperature, gas-phase, electron diffraction study of *p*-xylylene⁹ has verified that the carbon skeletal framework is essentially quinoid (**1**, $r_g(\text{C}=\text{C})_{\text{ave}} = 1.382$ (11) Å,¹⁰ $r_g(\text{CH}-\text{CH}) = 1.462$ (7) Å). The slight lengthening of the double bonds (mean electron diffraction value of double bonds:¹¹ $r_g(\text{C}=\text{C}) = 1.34$ Å) may be related to the proposed diradical contribution.

Thiele synthesized the first isolable derivative of *p*-xylylene (**3**) in 1904, after attempts to prepare the unsubstituted compound failed.¹² Thiele's hydrocarbon reacts with oxygen, but can be manipulated without elaborate precautions. It has been examined by a variety of physical methods,¹³ and there seems to be little doubt that the molecule has a singlet ground state. One might expect the phenyl substituents to shift the structure of **3** toward



the diradicaloid end of the structural spectrum. A major goal of the present research was to obtain a high-quality, single-crystal X-ray structure of Thiele's hydrocarbon to probe the extent that

(1) 3,6-Bis(methylene)-1,4-cyclohexadiene, also called *p*-quinodimethane.

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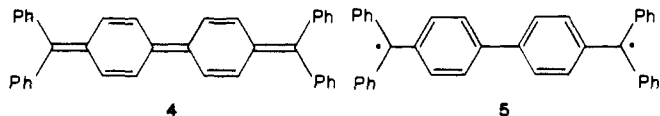
(10) It was not possible to resolve the two closely spaced double bond distances, and an average distance was reported. Although the *p*-xylylene was generated by the thermolysis of [2,2]paracyclophane at 750 °C, the bond distances reported here are extrapolated to 25 °C.

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the phenyl substituents impart diradicaloid characteristics to the molecule. Such a study also provides an opportunity for working out the experimental procedures for handling the homologous, highly reactive, and far more interesting molecule, Chichibabin's hydrocarbon (4).



Shortly after Gomberg's preparation of the triphenylmethyl radical in 1900,¹⁴ Chichibabin attempted to synthesize the analogous diradical **5**.¹⁵ He obtained a blue-violet compound that reacted avidly with oxygen, yielding a polymeric peroxide. Considering the oxygen sensitivity of the molecule and the available methodology, Chichibabin provided reasonable evidence that he had prepared the $C_{38}H_{28}$ hydrocarbon. Early experimental studies on Chichibabin's hydrocarbon led to speculation as to whether it existed as a singlet, a triplet, or a mixture of the two spin states.^{16,17,13a-h} Preparations of **4** catalyze the interconversion of ortho and para hydrogen,^{13b} a classical test for unpaired spins. On the other hand, magnetic susceptibility measurements favor a singlet ground state.^{13a} ESR spectroscopy^{18,13f,g} should, in principle, be able to resolve the question, but the research in this area to date has been plagued with paradox,^{18d} controversy, and inconsistencies.^{17,18,13f,g} Numerous attempts to observe triplet spectra in solution have failed; a doublet spectrum is invariably found, however.^{18,13f,g} Recently, this signal has been unambiguously attributed to a para-substituted biphenyldiphenylmethyl radical,^{18f,g,i,j} which presumably arises from (1) the generation of only one radical center in the synthesis of Chichibabin's hydrocarbon, (2) a side reaction (e.g., reaction with dioxygen or a hydrogen atom donor) that leaves one radical center intact, or (3) a dimerization process that yields a diradical whose spins are too far apart to communicate effectively. To complicate the picture, a solid-state triplet signal has been reported^{18f} for a powder sample of hydrocarbon **4**. It is believed that the observed triplet lies about 5.5 kcal/mol above a singlet state.^{18f}

A recent critical review¹⁷ has discussed existing experimental inconsistencies and makes a reasonable case for the assignment of a singlet ground state to Chichibabin's hydrocarbon. In the present work an X-ray crystal structure of this molecule was undertaken to probe the ground-state multiplicity by a significantly different method than had been used to the present. In the most favorable case, a high quality X-ray structure might provide a definitive solution to this long-standing question. In the minimum, it should yield a detailed mapping of the structure of this fascinating organic molecule.

Results and Discussion

Thiele's Hydrocarbon (3). A synthetic approach similar to that of Thiele¹² yielded the hydrocarbon with little difficulty. The final

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Table I. Fractional Coordinates and Isotropic Thermal Parameters (\AA^2) for Thiele's Hydrocarbon (-157°C)^a

atom	x	y	z	B_{iso}^b
C(1)	905 (2)	-1385 (3)	10723 (4)	19
C(2)	6 (2)	1680 (3)	9219 (4)	18
C(3)	990 (2)	327 (3)	9958 (4)	18
C(4)	1927 (2)	684 (3)	9981 (4)	17
C(5)	2973 (2)	-465 (3)	11229 (4)	17
C(6)	3766 (2)	-838 (3)	10206 (4)	18
C(7)	4740 (2)	-1943 (3)	11304 (4)	21
C(8)	4961 (2)	-2690 (3)	13476 (4)	23
C(9)	4206 (2)	-2300 (3)	14562 (4)	24
C(10)	3229 (2)	-1195 (3)	13465 (4)	21
C(11)	1943 (2)	2249 (3)	8701 (4)	17
C(12)	2646 (2)	3453 (3)	9875 (5)	20
C(13)	2704 (2)	4877 (3)	8678 (5)	23
C(14)	2065 (2)	5128 (3)	6288 (5)	26
C(15)	1371 (2)	3939 (3)	5094 (5)	26
C(16)	1308 (2)	2510 (3)	6285 (4)	21
H(1)	152 (2)	-241 (3)	1111 (4)	23 (5)
H(2)	3 (2)	286 (3)	874 (4)	16 (5)
H(3)	360 (2)	-28 (3)	863 (4)	18 (5)
H(4)	525 (2)	-217 (3)	1047 (4)	31 (6)
H(5)	567 (2)	-350 (3)	1427 (4)	19 (5)
H(6)	437 (2)	-282 (3)	1608 (5)	28 (5)
H(7)	270 (2)	-91 (3)	1423 (4)	21 (5)
H(8)	309 (2)	329 (3)	1151 (4)	17 (5)
H(9)	319 (2)	567 (3)	952 (4)	24 (5)
H(10)	210 (2)	612 (4)	538 (4)	29 (5)
H(11)	90 (2)	413 (4)	342 (5)	36 (6)
H(12)	82 (2)	166 (3)	544 (4)	14 (5)

^a Fractional coordinates are $\times 10^4$ for carbon atoms and $\times 10^3$ for hydrogen atoms. B_{iso} values are $\times 10$. ^b Isotropic values for those atoms refined anisotropically (without error limits) were calculated by using the formula given by Hamilton (ref 26).

Table II. Key Bond Distances (\AA) for Thiele's Hydrocarbon (-157°C)^a

A	B	dist	A	B	dist
C1	C2	1.346 (3)	C7	C8	1.382 (3)
C1	C3'	1.449 (3)	C8	C9	1.382 (4)
C2	C3	1.449 (3)	C9	C10	1.382 (4)
C3	C4	1.381 (3)	C11	C12	1.396 (3)
C4	C5	1.479 (3)	C11	C16	1.395 (3)
C4	C11	1.484 (3)	C12	C13	1.388 (3)
C5	C6	1.403 (3)	C13	C14	1.383 (4)
C5	C10	1.401 (3)	C14	C15	1.382 (4)
C6	C7	1.380 (3)	C15	C16	1.391 (3)

^a Atom-numbering system from Figure 1.

Table III. Selected Bond Angles (deg) for Thiele's Hydrocarbon^a

A	B	C	angle
C1	C2	C3	122.87 (22)
C1	C3'	C2'	114.24 (20)
C2	C3	C4	122.08 (21)
C3	C4	C5	122.95 (20)
C5	C4	C11	115.46 (19)
C4	C5	C6	120.25 (20)
C5	C6	C7	121.38 (22)
C6	C7	C8	120.27 (23)

^a Atom-numbering system from Figure 1.

step involved a 1,6-debromination of 1,4-bis(diphenylbromomethyl)benzene with zinc. Bright orange-yellow prisms of **3** were obtained which were suitable for single-crystal X-ray analysis. Solutions of **3** fluoresce and are slightly oxygen and light sensitive.

The X-ray data were acquired at -157°C ; the structure was solved by direct methods and refined by full-matrix, least-squares analysis. All the hydrogens were located and refined isotropically. The final R-factor was 0.038, and the estimated standard deviations (esds) for the bonded carbons were in the 0.003-0.004 \AA range. The fractional coordinates and isotopic thermal parameters are given in Table I. Selected bond distances and bond angles are provided in Tables II and III. An ORTEP view of Thiele's

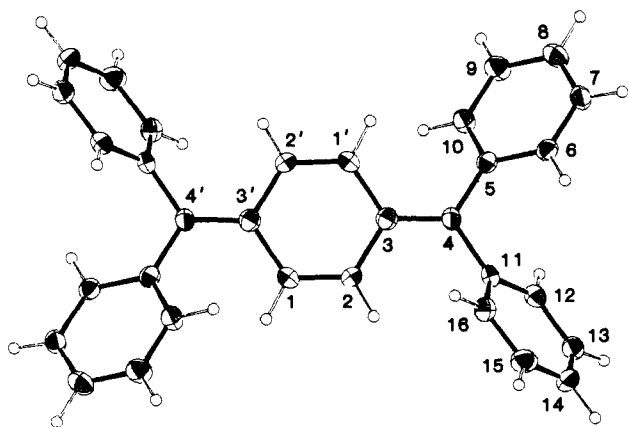


Figure 1. An ORTEP drawing of Thiel's hydrocarbon showing the atom-numbering scheme.

hydrocarbon that shows the atom-numbering scheme used in the tables is shown in Figure 1. The esds are listed in parentheses.

The bond distances and bond angles in **3** that are chemically equivalent are all within the tabulated one σ error limits. The eight carbons of the *p*-xylylene system are essentially coplanar (largest deviation of any atom 0.015 Å). As might be expected, the sterically congested phenyl groups are displaced out of the main plane (Figure 1). The molecule possesses C_i symmetry and has two different phenyl torsional angles (37.8° and 48.8°, average value 43.3°). The terminal methylene groups are also twisted a small extent (13.9°).

There is well-defined bond alternation in the *p*-xylylene framework. The bond lengths in this portion of the molecule (1.346 (3) and 1.449 (3) Å) differ substantially from the aromatic mean (approximately 1.39 Å for this substitution pattern¹⁹). The exo methylene double bonds (1.381 (3) Å) are about 0.04–0.05 Å longer than those in typical olefins (1.33–1.34 Å^{20,24}). All of the carbon–carbon distances are roughly comparable to the electron diffraction values for *p*-xylylene.⁹ In the electron diffraction experiment, it was impossible to resolve the two double-bonded distances because of their close spacing; an average value of $r_g = 1.382$ (11) Å (3 σ error limit) was obtained. C2C3 was $r_g = 1.462$ (7) Å. Considering that the structures were carried out 900 °C apart (–157 and 750 °C), that electron diffraction and X-ray structural parameters are defined differently,²¹ and the influence of crystal-lattice vibrations,²³ the small discrepancies in the two sets of parameters are probably not worth pondering at length. The main point to be drawn from the above comparisons is clear: the phenyl groups exert no major influence on the carbon–carbon distances. This is not surprising considering the twisted conformation of the four substituents. The structure is highly suggestive from the chemical point of view. The increased kinetic stability of Thiele's hydrocarbon relative to *p*-xylylene appears to be largely steric in origin. Semiempirical molecular orbital calculations support this inference.²⁴

Chichibabin's Hydrocarbon (4). In synthesizing hydrocarbon **4**, several modifications of existing procedures were attempted. Some were successful; some were not. 4,4'-Bis(diphenyl-

Table IV. Fractional Coordinates and Isotropic Thermal Parameters (Å²) for Chichibabin's Hydrocarbon (–159 °C)^a

atom	x	y	z	B_{iso}^b
C(1)	4312 (2)	189 (2)	9883 (2)	17
C(2)	4047 (2)	1044 (2)	10603 (2)	19
C(3)	2747 (2)	1418 (2)	10356 (2)	19
C(4)	1575 (2)	976 (2)	9337 (2)	18
C(5)	1847 (2)	120 (2)	8615 (2)	19
C(6)	3144 (2)	–266 (2)	8898 (2)	19
C(7)	219 (2)	1339 (2)	9056 (2)	19
C(8)	–186 (2)	1954 (2)	10097 (2)	19
C(9)	–1236 (2)	2663 (2)	9628 (3)	22
C(10)	–1712 (2)	3178 (2)	10597 (3)	26
C(11)	–1144 (3)	3020 (2)	12042 (3)	27
C(12)	–84 (2)	2344 (2)	12541 (3)	24
C(13)	392 (2)	1808 (2)	11582 (2)	21
C(14)	–850 (2)	1107 (2)	7681 (2)	20
C(15)	–562 (2)	1145 (2)	6377 (2)	23
C(16)	–1581 (3)	961 (2)	5084 (3)	26
C(17)	–2901 (3)	733 (2)	5067 (3)	27
C(18)	–3200 (2)	673 (2)	6340 (3)	25
C(18)	–2187 (2)	856 (2)	7633 (3)	22
H(1)	484 (3)	136 (2)	1124 (3)	26 (6)
H(2)	263 (3)	207 (2)	1083 (3)	24 (6)
H(3)	105 (3)	–26 (2)	789 (3)	30 (6)
H(4)	329 (3)	–89 (2)	848 (3)	31 (6)
H(5)	–164 (3)	278 (2)	863 (3)	22 (5)
H(6)	–241 (3)	367 (2)	1025 (3)	33 (7)
H(7)	–145 (3)	336 (2)	1272 (3)	38 (7)
H(8)	31 (3)	225 (2)	1349 (3)	26 (6)
H(9)	112 (3)	133 (2)	1197 (3)	24 (6)
H(10)	33 (3)	131 (2)	639 (3)	36 (7)
H(11)	–145 (3)	105 (2)	421 (3)	27 (6)
H(12)	–358 (3)	66 (2)	423 (3)	26 (6)
H(13)	–402 (3)	54 (2)	637 (3)	37 (7)
H(14)	–240 (3)	85 (2)	847 (3)	21 (5)

^a Fractional coordinates are $\times 10^4$ for carbon atoms and $\times 10^3$ for hydrogen atoms. B_{iso} values are $\times 10$. ^b Isotropic values for those atoms refined anisotropically (without error limits) were calculated by using the formula given by Hamilton (ref 26).

Table V. Key Bond Distances (Å) for Chichibabin's Hydrocarbon^a

A	B	dist	A	B	dist
C1	C1'	1.448 (4)	C8	C13	1.408 (3)
C1	C2	1.420 (3)	C9	C10	1.386 (3)
C1	C6	1.420 (3)	C10	C11	1.375 (4)
C2	C3	1.372 (3)	C11	C12	1.381 (4)
C3	C4	1.429 (3)	C12	C13	1.393 (3)
C4	C5	1.424 (3)	C14	C15	1.407 (3)
C4	C7	1.415 (3)	C14	C19	1.397 (3)
C5	C6	1.371 (3)	C15	C16	1.392 (3)
C7	C8	1.457 (3)	C16	C17	1.381 (4)
C7	C14	1.482 (3)	C17	C18	1.383 (4)
C8	C9	1.402 (3)	C18	C19	1.389 (3)

^a Atom-numbering system from Figure 2.

hydroxymethyl)biphenyl was obtained by treating 4,4'-dibromobiphenyl with 2 mol of *n*-butyllithium, followed by 2 mol of benzophenone. No problems were encountered in converting the resulting diol to a dibromide. The subsequent zinc debromination to Chichibabin's hydrocarbon went in poor yield. This was not appreciated at first, because solutions of hydrocarbon **4** are blue-violet and intensely colored (λ_{max} 574 nm, ϵ_{max} 1.05×10^5). The zinc debromination route was attempted because it had worked so well in the preparation of Thiele's hydrocarbon. Control experiments showed that the zinc reacts smoothly with the dibromide, but it also destroys the hydrocarbon. An alternative procedure²⁵ employing the dichloride and mercury provided large crystals of Chichibabin's hydrocarbon in high yield. The final dechlorination reaction was carried out by using vacuum line procedures, and the isolated solid was stored and manipulated in a nitrogen atmosphere dry box.

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(21) The most directly comparable electron diffraction parameter is probably r_a (ref 22). The r_a values for *p*-xylylene are the following: r_a (C=C)_{ave} = 1.363 Å, r_a (CH–CH) = 1.441 Å.

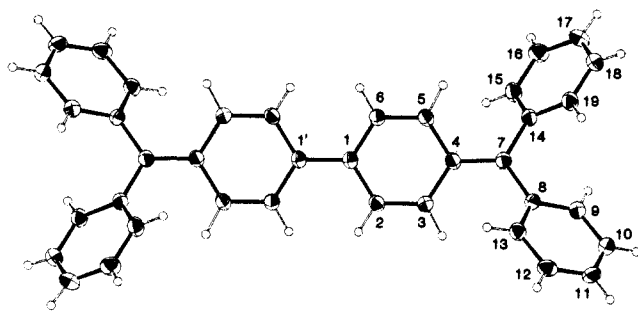
(22) Kuchitsu, K. In *Diffraction Studies on Non-Crystalline Substances*; Hargittai, I., Orville-Thomas, W. T., Eds.; Elsevier: Amsterdam, 1981; pp 63–116.

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Table VI. Selected Bond Angles (deg) for Chichibabin's Hydrocarbon^a

A	B	C	angle
C1'	C1	C2	122.29 (24)
C2	C1	C6	115.94 (18)
C1	C2	C3	122.36 (20)
C2	C3	C4	121.73 (20)
C3	C4	C5	115.69 (19)
C3	C4	C7	123.34 (20)
C4	C7	C8	122.07 (19)
C8	C7	C14	117.69 (18)
C7	C8	C9	120.38 (20)
C8	C9	C10	120.76 (22)
C9	C10	C11	120.69 (24)

^a Atom-numbering system from Figure 2.**Figure 2.** An ORTEP drawing of Chichibabin's hydrocarbon showing the atom-numbering scheme.

The solid hydrocarbon is remarkable. It is bright green and has a pronounced metallic luster. Crystals of **3** are less reactive with oxygen than are the blue-violet solutions, which are bleached rapidly by air. Sealed, degassed solutions of **4** are stable indefinitely at room temperature. A Beer's law study was conducted over the concentration range 3.63×10^{-6} – 3.63×10^{-3} M, which is the highest concentration that could be prepared reproducibly. More concentrated solutions than this were obtained in the final step of the synthesis of **4**; presumably they were supersaturated. No dimerization of **4** was detected from the Beer's law plot over this limited concentration range.

The X-ray crystallographic data for Chichibabin's hydrocarbon were collected at -159°C . The data analysis was straightforward. All of the hydrogens were located and refined isotropically. The R-factor was not quite as good (0.052) as for Thiele's hydrocarbon, but the esds for the bonded carbons were similar. Fractional coordinates and isotropic thermal parameters for Chichibabin's hydrocarbon are recorded in Table IV. Selected bond distances and bond angles are given in Tables V and VI. An ORTEP view of the molecule providing the atom-numbering scheme used in Tables IV–VI is shown in Figure 2.

As was the case with Thiele's hydrocarbon, there is excellent agreement among chemically equivalent structural parameters. The most striking conformational feature is the planarity of the central rings. No atom lies farther than 0.016 \AA out of the least-squares plane of the 14 di-*p*-xylylene carbons. Whether this conformation is also preferred in solution is not clear. Biphenyl is flat or nearly so in the crystalline state,^{27,28} but its rings form a dihedral angle of $44.4 (1.2)^\circ$ in the gas phase.²⁹ The four phenyl substituents on Chichibabin's hydrocarbon are positioned very much like those on Thiele's hydrocarbon (*C_i* symmetry also). They are rotated an average of 36.9° (two different angles, 32.0° and

41.9°), and the terminal methylene groups are twisted 22.7° .

The carbon-carbon bond lengths of the middle portion of Chichibabin's hydrocarbon are the most interesting. There is still bond alternation, but it is less distinct than in Thiele's hydrocarbon. The three bond distances in the rings (C1C2, C2C3, and C3C4) are all closer to mean aromatic values ($1.420 (3)$, $1.372 (3)$, and $1.429 (3) \text{ \AA}$, respectively). The most unusual distances are those of the exo methylene groups C4C7 and C1C1'. Both are written as double bonds in canonical structure **4**. At $1.415 (3)$ and $1.448 (4) \text{ \AA}$, respectively, they are far from normal. The C4C7 bond is 0.03 \AA longer than the corresponding bond (C3C4, $1.381 (3) \text{ \AA}$) in Thiele's hydrocarbon. Moreover, the torsional angle at C4C7 (22.7°) is almost twice that of C3C4 (13.9°) in Thiele's hydrocarbon. This must be due, at least in part, to diminished π -bonding between C4 and C7 and a lower torsional force constant. The increased rotation about C4C7 is very likely coordinated with a reduction in the angles in the phenyl groups (32.0° and 41.9° vs. 37.8° and 48.4° for Thiele's hydrocarbon). This point is discussed further below.

The bond between C1 and C1' is particularly intriguing. It is over 0.1 \AA longer than the characteristic double bond average, but it is still short of the aryl-aryl single bond distance in biphenyl (X-ray,^{27b} $1.493 (3) \text{ \AA}$; neutron diffraction,^{27c} 1.495 \AA). Apparently there is still some π -bonding between C1 and C1'. Caution should be exercised in assessing the extent of bonding at this site, however, because the bond is probably stretched slightly by the buttressing of the hydrogens attached to C2', C6, C2, and C6'. These nonbonded interactions were estimated by two methods and found to be severe. The distance between the least-squares positions of the interacting ortho hydrogens is 1.96 \AA . Alternatively, the H...H distance can be estimated by placing the hydrogens 1.08 \AA (ref 20) away from the carbons along the experimental C-H bond vectors and is even shorter (1.83 \AA). In either case, the buttressing hydrogens are closer than the sum of their van der Waals radii (2.34 – 2.4 \AA , ref 30 and 31). Nevertheless, while steric effects undoubtedly play a role in determining the C1C1' bond length, they are probably not the dominant factor. Double bonds are difficult to lengthen appreciably through steric interactions.³² This assertion is discussed quantitatively in a subsequent section on molecular mechanics calculations.

At least two hypotheses can be offered to rationalize the unique bond lengths in Chichibabin's hydrocarbon. The first is that both singlet and triplet species are packed randomly into the crystal. In such a case the observed structure would be an average of the two composite structures (**4** and triplet **5**). As **5** is blended with **4**, the bonds in the internal six-membered rings shift toward 1.39 \AA , and C4C7 and C1C1' are lengthened. The 1969 solid-state ESR study,^{18f} which found less than one percent of the triplet state at 20°C , argues against this alternative. Since the overall ESR picture is still not completely harmonious, however, it was felt that this alternative should be carefully scrutinized. The second hypothesis is that the X-ray crystallographic sample is a singlet species, but that a diradical contribution **5** is mixed into the ground-state wave function. If typical bond lengths are assigned to the two limiting structural forms **4** and **5**, the relative fractions of the two forms can be estimated from the X-ray crystallographic data. When this is done on a bond-by-bond basis³³ for the di-*p*-xylylene framework, it is found that the average diradical contribution is over 60%.

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(31) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, 1960; p 260.

(32) (a) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 5734. (b) Ermer, O.; Lifson, S. *J. Am. Chem. Soc.* **1973**, *95*, 4121. (c) Engler, E. M.; Andose, J. D.; von R. Schleyer, P. *J. Am. Chem. Soc.* **1973**, *95*, 8005. (d) Ermer, O. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 658.

(33) The assumed limiting bond lengths were as follows: $r(\text{C}=\text{C}) = 1.46 \text{ \AA}$ (ref 34), $r(\text{C}-\text{C}) = 1.33 \text{ \AA}$ (ref 34), $r(\text{C}_{\text{Ar}}=\text{C}_{\text{Ar}}) = 1.39 \text{ \AA}$ (ref 34), $r(\text{C}_{\text{Ar}}-\text{C}_{\text{Ar}}) = 1.51 \text{ \AA}$ (ref 27), $r(\text{C}_{\text{Ar}}-\text{C}^*) = 1.47 \text{ \AA}$ (ref 35).

(34) Dunitz, J. D. *X-ray Analysis and the Structure of Organic Molecules*; Cornell University Press: Ithaca, 1979; p 338.

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(27) (a) Charbonneau, G.-P.; Delugard, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1976**, *32B*, 1420. (b) Charbonneau, G.-P.; Delugeard, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1977**, *33B*, 1586. (c) Cailleau, H.; Baudour, J. L.; Zeyen, C. M. E. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *35B*, 426.

(28) See ref 29 for a recent review of solid-state, gas-phase, and solution studies of biphenyl.

(29) Almendinger, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J.; Samdal, S. *J. Mol. Struct.* **1985**, *128*, 59.

Table VII. Anisotropic Thermal Parameters (\AA^2)^a for Chichibabin's Hydrocarbon^b

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	21 (1)	24 (1)	20 (1)	1 (1)	6 (1)	3 (1)
C(2)	21 (1)	28 (1)	21 (1)	-1 (1)	5 (1)	-1 (1)
C(3)	22 (1)	26 (1)	23 (1)	1 (1)	6 (1)	-4 (1)
C(4)	20 (1)	27 (1)	21 (1)	1 (1)	6 (1)	0 (1)
C(5)	20 (1)	28 (1)	24 (1)	-1 (1)	6 (1)	0 (1)
C(6)	22 (1)	22 (1)	26 (1)	0 (1)	7 (1)	-1 (1)
C(7)	21 (1)	28 (1)	24 (1)	1 (1)	7 (1)	-1 (1)
C(8)	21 (1)	27 (1)	25 (1)	0 (1)	10 (1)	-5 (1)
C(9)	24 (1)	31 (1)	27 (1)	2 (1)	7 (1)	-3 (1)
C(10)	25 (1)	31 (1)	42 (1)	2 (1)	10 (1)	-9 (1)
C(11)	31 (1)	38 (1)	38 (1)	-4 (1)	17 (1)	-17 (1)
C(12)	31 (1)	38 (1)	24 (1)	-9 (1)	12 (1)	-7 (1)
C(13)	23 (1)	27 (1)	28 (1)	-2 (1)	8 (1)	0 (1)
C(14)	21 (1)	29 (1)	23 (1)	3 (1)	5 (1)	-2 (1)
C(15)	22 (1)	37 (1)	28 (1)	1 (1)	8 (1)	0 (1)
C(16)	36 (1)	39 (1)	23 (1)	-2 (1)	11 (1)	-3 (1)
C(17)	30 (1)	39 (1)	29 (1)	-5 (1)	1 (1)	-7 (1)
C(18)	23 (1)	35 (1)	36 (1)	-3 (1)	8 (1)	-7 (1)
C(19)	24 (1)	32 (1)	28 (1)	1 (1)	10 (1)	0 (1)

^aAll values $\times 10^3$. ^bForm of the anisotropic thermal parameters is $\exp[-2\pi^2(h^2a^2U_{11} + hkabU_{12} + \dots)]$.

Table VIII. Comparison of Selected Carbon Skeletal Bond Distances (\AA) at Various Temperatures ($^\circ\text{C}$)^a

bond dist	-159, $^\circ\text{C}$	-50, $^\circ\text{C}$	+20, $^\circ\text{C}$
C1C1'	1.448 (4)	1.453 (8)	1.458 (9)
C1C2	1.420 (3)	1.418 (6)	1.409 (7)
C2C3	1.372 (3)	1.375 (6)	1.354 (7)
C3C4	1.429 (3)	1.419 (6)	1.417 (6)
C4C7	1.415 (3)	1.430 (6)	1.421 (6)

^aAtom-numbering system from Figure 2.

An obvious experimental test of the two explanations is to look at the anisotropic thermal parameters of the di-*p*-xylylene carbons. These are provided in Table VII. The thermal parameters for atoms 1-7 are essentially isotropic. If two different species are present, they must be much closer in structure than the assumed limiting models.³³

In an effort to change the relative concentrations of **4** and **5** (first hypothesis), the single crystal of Chichibabin's hydrocarbon was raised to -50 and 20 $^\circ\text{C}$, and the structures were redetermined. The resulting bond distances are shown in Table VIII. The error limits are larger at the higher temperatures, but there are no systematic trends that support the two species alternative.

One final experimental test that was applied to the two explanations was to repeat the solid-state ESR experiment with the same batch of crystals utilized in the X-ray studies. It seems desirable to examine the magnetic properties of Chichibabin's hydrocarbon in a case where the crystal and molecular structures were unambiguously established. The previous ESR work^{18f} specified only that the samples were microcrystalline and that powder spectra were taken. In synthesizing Chichibabin's hydrocarbon via several different routes for the present experiments, it was observed that it is far more common to obtain violet powders than beautiful green crystals. The potential for occluding paramagnetic impurities seemed much greater for the powders.

Crystals that were slightly larger than coarse table salt, yet clearly discernible as similar to those used in the X-ray experiments, were selected for the ESR sample. Like all previous ESR studies of Chichibabin's hydrocarbon, the sample afforded a doublet spectrum (25 $^\circ\text{C}$). The peak width was 5 G. In contrast to the earlier work of Brauer et al.,^{18f} no triplet resonance peaks were seen on the wings of the monoradical signal, even with time averaging.³⁶ The reported triplet splittings were 288 G.^{18f} The ESR spectrum of Chichibabin's hydrocarbon was rerecorded at -196 $^\circ\text{C}$, and the results were exactly the same. A clear-cut explanation cannot be offered for the conflicting observations at

(36) The ESR measurements were carried out by Professor Mathew S. Platz (Department of Chemistry, The Ohio State University).

Table IX. Comparison of Selected Molecular Mechanics and X-ray Structured Parameters for Thiele's Hydrocarbon

bond (\AA)	MM ^a	X-ray	MM-XR ^b
C1C2	1.357	1.346 (3)	0.011
C2C3	1.459	1.449 (3)	0.010
C3C4	1.374	1.381 (3)	-0.007
C4C5	1.484	1.479 (3)	0.005
C _{Ar} C _{Ar} ^c	1.398	1.389	0.009
angle (deg)	MM	X-ray	MM-XR
$\angle\text{C1C2C3}$	122.09	122.88 (22)	-0.79
$\angle\text{C2C3C1}'$	115.79	114.24 (20)	1.55
$\angle\text{C6C5C10}$	118.74	117.10 (22)	1.64
$\angle\text{C5C6C7}$	120.76	121.38 (22)	-0.62
$\angle\text{C6C7C8}$	120.02	120.27 (23)	-0.25
$\angle\text{C7C8C9}$	119.73	119.60 (23)	0.13
C3C4	8.62 ^d	13.87	-5.25
C7C8, C7C14	49.90 ^e	43.37 ^f	6.53

^aFully optimized molecular mechanics structure. ^bMolecular mechanics X-ray difference. ^cAverage aromatic value. ^dMaximum deviation for individual torsional angles $\pm 0.2^\circ$. ^eMaximum deviation for individual torsional angles $\pm 1.5^\circ$. ^fAverage experimental value.

the present time. It may be related to sample preparation or an assortment of other factors. Fortunately, as far as the present discussion is concerned, it is unnecessary to resolve these contradictory results. Both ESR studies are consistent with there being little or no triplet at -159 $^\circ\text{C}$.

The experimental evidence presented above strongly suggests that Chichibabin's hydrocarbon exists largely or exclusively in the singlet form at -159 $^\circ\text{C}$. The unusual bond lengths are apparently a manifestation of diradical character. Molecular mechanics calculations are consistent with this point of view.

Molecular Mechanics Studies. The X-ray studies of Thiele's and Chichibabin's hydrocarbons show several interesting structural features (e.g., the minimal influence of the phenyl groups on the *p*-xylylene nucleus in Thiele's hydrocarbon, the planarity of the di-*p*-xylylene ring system, and the unusually long C1C1' and C4C7 bond lengths in Chichibabin's hydrocarbon). In an attempt to sort out the factors that are important in determining the solid-state geometries of the two hydrocarbons, the free equilibrium structures for both molecules were modeled by the molecular mechanics (MM) method.³⁷ The MM program of Gilbert and Gajewski (GG)³⁸ was employed in these calculations. The MM approach was selected for several reasons. Meaningful ab initio MO calculations were out of the question because of the size of the molecules. Chichibabin's hydrocarbon was also too large to handle employing the MNDO⁴¹ semiempirical MO method without making extensive modifications of our usual programs.⁴² A MM procedure capable of adequately treating the aromatic rings and double bonds seemed like a reasonable alternative. The GG program constructs a force field for the π -system starting from a variable electronegativity self-consistent field (VESCF) MO calculation (Allinger, MMP1, ref 38). The VESCF method was originally introduced by Brown⁴³ and was developed by Allinger.⁴⁴

(37) Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, 1983.

(38) The MM program of K. E. Gilbert and J. J. Gajewski (Department of Chemistry, Indiana University) handles a variety of functional groups and is available in VAX and IBM PC versions. The calculations reported here were carried out on a VAX 11/780 computer. In dealing with conjugated hydrocarbons, the GG program utilizes the parameterization of Allinger's MM2 (ref 39) and MMP1 (π -electron calculation, ref 40) programs.

(39) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127.

(40) Allinger, N. L.; Sprague, J. T. *J. Am. Chem. Soc.* **1973**, *95*, 3893.

(41) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899.

(42) The MNDO option of the program MNDOC (W. Thiel, Quantum Chemistry Exchange Program, No. 438, Department of Chemistry, Indiana University) was redimensioned to accommodate Thiele's hydrocarbon (C₃₂H₂₄) on a CDC 855 computer. A constrained structure was obtained for comparison purposed by holding the phenyl group and the C3C4 torsional angles at their average experimental values (ref 24). All of the carbon-carbon bond lengths were within 0.015 \AA of the MM results. Agreement with the X-ray parameters was not as good, however. Extensive modifications of MNDOC would have been necessary in order to handle Chichibabin's hydrocarbon (C₃₃H₂₈).

(43) Brown, R. D.; Heffernan, M. L. *Aust. J. Chem.* **1959**, *12*, 319.

Table X. Comparison of Selected Molecular Mechanics and X-ray Structural Parameters for Chichibabin's Hydrocarbon

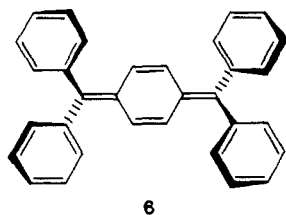
bond (Å)	MMO ^a	MMC ^b	X-ray	MMC-XR
C1C1'	1.403	1.401	1.448 (4)	-0.047
C1C2	1.444	1.454	1.420 (3)	0.034
C2C3	1.365	1.362	1.372 (3)	-0.010
C3C4	1.444	1.448	1.429 (3)	0.019
C4C5	1.445	1.448	1.424 (3)	0.024
C5C6	1.365	1.362	1.371 (3)	-0.009
C1C6	1.444	1.455	1.420 (3)	0.035
C4C7	1.383	1.377	1.415 (3)	-0.038
C _{Ar} C _{Ar} ^c	1.398	1.398	1.391	0.007
angle (deg)	MMO	MMC	X-ray	MMC-XR
∠C2C3C4	120.75	121.38	121.73 (20)	-0.60
∠C2C1C6	117.25	114.72	115.94 (18)	-1.22
∠C3C4C5	118.00	116.60	115.69 (19)	0.59
C1C1'	24.52	0	0.58	-0.58
C4C7	33.01	25.30	22.70	2.60
C7C8, C7C14	45.50	51.11	36.91 ^d	14.20

^aOptimized structure with D_2 symmetry. ^bBond C1C1' constrained to enforce planarity, C_{2h} symmetry. ^cAverage aromatic value. ^dAverage experimental value.

In addition to handling a molecule the size of chichibabin's hydrocarbon, the MM mechanics approach had the added advantage of treating steric factors as well as any theoretical or semiempirical method.

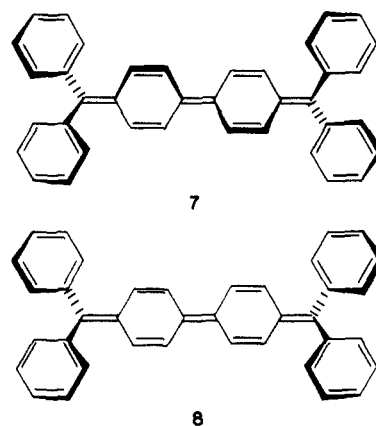
A minor problem was encountered in searching for global minima for both compounds. In each case several minimum energy geometries were found that differed mainly in terms of the relative positioning and exact torsional angles of the phenyl groups. Because of the considerable computational time involved, completely systematic searches were not carried out. Enough conformations were explored to show that the phenyl group torsional angles were near their optimum values. An important observation was made in searching for the best structures, namely that the *p*-xylylene and di-*p*-xylylene bond distances are moderately insensitive to torsional angle changes.

The final MM structure for Thiele's hydrocarbon is summarized in Table IX. The four phenyl torsional angles are similar but not identical ($\pm 1.5^\circ$). The resulting near- D_2 symmetry **6** is higher than that found in the experimental structure.

**6**

Preliminary calculations on Chichibabin's hydrocarbon revealed that the conformation of lowest energy also had D_2 symmetry. Accordingly, the geometry was constrained to the symmetry of **7** to facilitate convergence (Table X, MMO). Since the di-*p*-xylylene portion of structure **7** was nonplanar, a second MM model was explored in which planarity was enforced on the central rings. C_{2h} symmetry was assumed for **8**, because it corresponded more closely to the conformation in the crystal (Table X, MMC).

The agreement between the MM-calculated bond distances and the corresponding X-ray crystallographic parameters for Thiele's hydrocarbon is exceptionally good (see MM-XR, Table IX). The largest value for MM-XR is a bit more than 0.01 Å. This is not much outside of 3σ error limits and is well within the expected inherent differences in the two methods. A comparison of the aromatic bond lengths illustrates the latter point nicely. Although the X-ray and MM averages differ by 0.009 Å (1.389 vs. 1.398 Å, respectively), they are both very close to the mean values of aromatic bond lengths obtained by the two procedures.^{19a,40} The

**7****8**

correspondence between the calculated and observed bond angles is also respectable (average absolute deviation of 0.8°). The largest discrepancies are in the torsional angles. Deficiencies in the MM procedure or crystal-packing forces are very likely responsible.

As expected, the lowest energy conformation of Chichibabin's hydrocarbon is twisted (24.5°) about C1C1' (conformation **7**, MMO, Table X) to alleviate the steric repulsions between the hydrogens at C2', C6, C2, and C6'. The H...H nonbonded distances in **7** (MMO) are increased to 2.25 Å. A second conformational point worth mentioning is that the phenyl torsional angles are larger than the average experimental values (MMO, 45.5° ; X-ray, 36.9°). In the MMC model the angles are even greater (MMC, 51.1°), and the C4C7 angle decreases to 25.3° (MMO, 33.0° ; X-ray, 22.7°). In all of the experimental and theoretical structures examined in this work, a rough correlation exists between the phenyl and C4C7 torsional angles; as one increases, the other decreases. This is a reasonable relationship, since the steric interactions of the phenyl groups are most easily relieved by some combination of twisting at these two sites.

Structural comparisons among the various carbon-carbon bond lengths are of the greatest interest. The average aryl distance as computed by MM is identical with that in Thiele's hydrocarbon (1.398 Å); the X-ray value is also similar (1.391 vs. 1.389 Å). In marked contrast, there are large differences between the calculated and experimental di-*p*-xylylene distances. Since the MMC model corresponds more closely to the X-ray conformation, MMC-XR is tabulated in Table X. The mean absolute value of MMC-XR is 3 times larger (0.03 Å) than the same quantity for Thiele's hydrocarbon. The largest deviations are for the most atypical bond lengths, C1C1' and C4C7 (0.047 and 0.038 Å, respectively). It is also important to note that bond alternation is more exaggerated in the theoretical structure. In viewing the deficiencies of the MMC model, the question arises as to why the geometry of Thiele's hydrocarbon is reproduced so well by the GG method and Chichibabin's so poorly. Although a number of explanations are conceivable, the most plausible is that the MM calculation does not properly account for the diradicaloid character of Chichibabin's hydrocarbon. There is no reason why the semiempirical VESCF MO procedure, which is mainly responsible for determining the carbon-carbon bond lengths, should be able to successfully treat such an unusual bonding situation. As a matter of fact, the only way that the GG procedure should reproduce the structural abnormalities is if they are steric in nature. One final point deserving comment in this connection is that steric effects do not appear to be the primary factor in lengthening C1C1', which is actually slightly longer in the twisted conformation (MMO, 1.403 Å) than in the planar form (MMC, 1.401 Å). This result seemed curious at first, but is reasonable upon reflection. The hydrogen-hydrogen nonbonded interactions should stretch the C1C1' bond a small amount in the MMC conformation; the MM results suggest that this is more than balanced by an increase in π - π overlap.

Crystal Packing. The luster of Chichibabin's hydrocarbon is extraordinary for an organic compound. Although it is known that metallic reflection does not necessarily connote additional

(44) (a) Allinger, N. L.; Tai, J. C. *J. Am. Chem. Soc.* **1965**, *87*, 2081. (b) Allinger, N. L.; Tai, J. C.; Stuart, T. W. *Theor. Chim. Acta.* **1967**, *8*, 101.

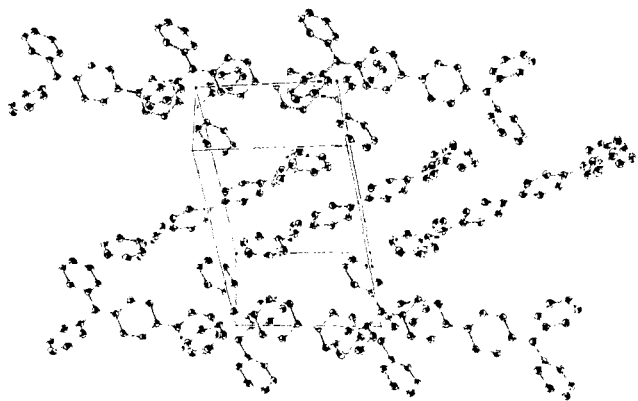


Figure 3. Packing diagram for Chichibabin's hydrocarbon. Two edge-centered chains (parallel edges) are omitted for clarity.

metallic characteristics,⁴⁶ it was felt that the crystal packing in this system was worth examining in view of the current interest⁴⁷ in the electrical properties of molecular crystals. Chichibabin's hydrocarbon belongs to the monoclinic space group $P2_1/n$. The packing diagram in Figure 3 reveals that the hydrocarbon molecules form chains, consisting of stacked, slightly overlapping units. One sequence of molecules passes through the center of the unit cell in the direction of the *a*-axis. Four more chains are located on the edges of the unit cell. Only two are shown in Figure 3 for clarity. The distance between the molecular planes in the stacks is 3.77 Å, although there are a number of carbon atom pairs that are much closer. A comparison of interplane and internuclear distances indicates that the hydrocarbon units are not perfectly aligned on top of one another. The terminal di-*p*-xylylene carbon (C7 of Figure 2) of one molecule is almost equidistant to the pair of terminal carbons in its nearest neighbor (C7...C7' = 4.14, C7...C4' = 4.17 Å, where the primes refer to a second molecule). This means that each unit in the chain is translated about 1.5 Å perpendicular to the interplane direction and the longest molecular axis. The edge chains in Figure 3 show this feature fairly well.

The closest carbon-carbon interactions within a chain are between the phenyl groups of one molecule and the di-*p*-xylylene system of the next unit. The shortest distance (C13...C5', 3.42 Å) is less than the sum of the van der Waals radii (Kitagorodsky,⁴⁸ 3.60; Bondi,⁴⁹ 3.54 Å). The closest interchain distances are between phenyl groups and are also quite short (C10...C17', 3.49 Å).

A negligible change (+0.04%) was noted in the unit cell dimension along the *a*-axis when Chichibabin's hydrocarbon was cooled from 20 to -159 °C. Conversely, a large decrease (-2.5%) was observed along the *b*-axis; the change in the *c*-direction was intermediate (-0.7%). Accordingly, cooling alters the interchain more than intrachain distances.

Further experiments on crystalline Chichibabin's hydrocarbon are planned. The influence, if any, of the small amount of monoradical contaminant (<1%) on the bright green color is being explored. It is also hoped that a suitable sample can be examined by polarized reflection spectroscopy.

Conclusions

The bond lengths in the central section of Thiele's hydrocarbon are similar to those in *p*-xylylene. This is not surprising considering

the fact that the four phenyl substituents are rotated an average of 43° out of a coplanar arrangement. In view of these structural findings, it is likely that the increased kinetic stability of Thiele's hydrocarbon relative to the parent is due mainly to steric effects. This conclusion may be of value in assessing the isolability of other $\alpha,\alpha',\alpha',\alpha'$ -tetrasubstituted *p*-xylylenes, where stability arguments have generally focused on the importance of resonance and polar effects.⁴⁵

The molecular symmetries of Chichibabin's and Thiele's hydrocarbons are the same (C_2) in the crystal systems studied here, although there are slight torsional angle differences. Since degassed solutions of Chichibabin's hydrocarbon are stable indefinitely at room temperature, it seems that the phenyl groups play a key role in making this molecule persistent also. Parallels between the two compounds end at this point, for Chichibabin's hydrocarbon is very oxygen sensitive. The most notable conformational feature of the molecule is the planarity of the di-*p*-xylylene ring system. Crystal packing forces are apparently responsible for the observed crystal preference.

The structural parameters of greatest significance in Chichibabin's hydrocarbon are the carbon-carbon distances. All of the bond lengths in the basic skeleton are intermediate between double and single bond values, ranging from 1.371-1.448 Å. Carbon-carbon linkages which are formally double bonds are up to 0.1 Å longer than anticipated.

The systematic consideration of several related pieces of evidence (the anisotropic thermal parameters of the carbons, a temperature dependence study of the bond distances, solid-state ESR measurements, and molecular mechanics calculations) indicates that the abnormal structural parameters are those of the ground state of Chichibabin's hydrocarbon but that there is an unusually large diradical contribution to the molecular wave function.

Experimental Section

General Methods. All melting points were determined with a Thomas Hoover melting point apparatus and are uncorrected. Spectra are included where they have not been reported previously or provide structural confirmation in cases where agreement with literature melting points is less than ideal. Infrared spectra were recorded on a Perkin Elmer 298 spectrophotometer. ¹H NMR spectra were obtained on either a Varian T-60A (60 MHz) or Varian EM390 (90 MHz) spectrometer. The ¹³C NMR spectrum was recorded on a Nicolet NT360 (360 MHz) spectrometer. All chemical shifts are reported in δ units with Si(CH₃)₄ as the internal standard unless otherwise stated. Sample preparations for Chichibabin's hydrocarbon were performed in a Vacuum Atmosphere's HE-553-2 drybox (nitrogen). UV-vis spectra were recorded on either a Perkin Elmer 552 or Perkin Elmer 330 spectrophotometer.

Materials. Carbon disulfide was distilled from P₂O₅ and stored over 4-Å molecular sieves. All other solvents and reagents were used as obtained from commercial sources without further purification. When drying was necessary, 4-Å molecular sieves were employed. Apiezon grease was used on all vacuum line and Schlenk equipment.

X-ray Crystallography, General Considerations. The diffractometer utilized for data collection was designed and constructed locally and has been described previously.⁵⁰ A Mo K α source ($\lambda = 0.71069$ Å) with a graphite monochromator supplied the radiation. All of the samples were maintained in an inert atmosphere at constant temperature (± 0.2 °C short term, ± 3 °C long term) employing a stream of dry nitrogen gas. The basic analysis procedures have been outlined.⁵⁰ The structures were solved by direct methods (MULTAN 78) and refined by full-matrix, least-squares analysis. All the hydrogens were located and refined isotropically.

Thiele's Hydrocarbon (3). A bright orange-yellow prism (0.09 × 0.17 × 0.12 mm) was mounted on a glass fiber with silicone grease (-157 °C). A systematic search of a limited hemisphere of reciprocal space revealed no systematic absences or extinctions, and the triclinic space group $P\bar{1}$ was assigned. Statistical tests and the solution and refinement of the structure confirmed this choice. The unit cell, $a = 13.881$ (7) Å, $b = 7.388$ (2) Å, $c = 5.963$ (2) Å, $\alpha = 98.45$ (3) Å, $\beta = 111.85$ (2)°, and $\gamma = 76.45$ (3)°, contained one molecule of **3** (C₃₂H₂₄) with a calculated density of $d = 1.232$ g/cm³. The final difference Fourier map was featureless, the largest peak being 0.17 e/Å³. The R factors for 1155

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reflections (77% of 1492 total reflections) with $|F_o| > 3\sigma(|F_o|)$ were $R = 0.038$ and $R_w = 0.040$.

Chichibabin's Hydrocarbon (4) a. Data at -159°C . A suitable fragment ($0.21 \times 0.21 \times 0.25$ mm) of a larger, metallic green crystal was mounted by using silicone grease. Preliminary analysis revealed diffraction maxima with $2/m$ symmetry and extinctions corresponding to the unique space group $P2_1/n$. The unit cell, $a = 10.243$ (3) Å, $b = 13.430$ (5) Å, $c = 9.851$ (3) Å, and $\beta = 108.34$ (2)°, contained two molecules of **4** ($\text{C}_{38}\text{H}_{24}$) with a calculated density of $d = 1.251$ g/cm³. The analysis was routine, and the final difference Fourier map was featureless, the largest peak being 0.19 e/Å³. The R factors for 3200 reflections (44% of 7231 total reflections) with $|F_o| > 2.33\sigma(|F_o|)$ were $R = 0.052$ and $R_w = 0.051$.

b. Data at -50°C . The crystal from part a was removed from the goniostat and immediately plunged into fingernail polish and mounted on a glass fiber. After drying, additional coats of polish were added to thoroughly encase the crystal. The cooling system was reset to -50°C . The preliminary analysis proceeded as above. The unit cell was now $a = 10.257$ (5) Å, $b = 13.636$ (8) Å, $c = 9.889$ (5) Å, and $\beta = 108.03$ (3)° and contained two molecules of **4** ($\text{C}_{38}\text{H}_{24}$) with a calculated density of $d = 1.224$ g/cm³. The R factors for 1772 reflections (50% of 3550 total reflections) with $|F_o| > 3\sigma(|F_o|)$ were $R = 0.084$ and $R_w = 0.084$.

c. Data at 20°C . The crystal of **4** was warmed to 20°C . The space group was the same. The unit cell changed slightly, $a = 10.238$ (5) Å, $b = 13.766$ (6) Å, $c = 9.922$ (4) Å, and $\beta = 107.73$ (2)°, and contained two molecules of **4** ($\text{C}_{38}\text{H}_{24}$) with a calculated density of $d = 1.208$ g/cm³. The R factors for 1136 reflections (33% of 3512 total reflections) with $|F_o| > \sigma(|F_o|)$ with $R = 0.063$ and $R = 0.065$.

Synthesis. Thiele's Hydrocarbon (3,6-Bis(diphenylmethylene)-1,4-cyclohexadiene, 3), a. 1,4-Bis(diphenylhydroxymethyl)benzene (**9**). Diol **9** was prepared from the reaction of phenylmagnesium bromide with dimethyl terephthalate, following the procedures of Thiele¹² and Vaughan^{13b} (50% yield): mp 160–163 °C (lit.^{13b} mp 170–171 °C).

b. 1,4-Bis(diphenylbromomethyl)benzene (**10**). Dibromide **10** was obtained by treating diol **9** with HBr in HOAc¹² (68% yield): mp 268–271 °C (lit.¹² mp 270–272 °C); ¹H NMR (90 MHz CDCl₃) δ 7.17 (s, 4 H), 7.30 (s, 20 H).

c. Hydrocarbon 3. One g (1.7×10^{-3} mol) of dibromide **10** and 0.4 g (6.1×10^{-3} mol) of activated zinc⁵¹ were added to 50 mL of benzene in a 100-mL, round-bottomed flask fitted with a reflux condenser with a nitrogen inlet tube. The flask was covered with aluminum foil, and the reaction and subsequent workup were conducted in subdued light. The solution was gently refluxed with magnetic stirring for 26.5 h. The resulting dark red solution was gravity filtered into an Erlenmeyer flask. The flask was stoppered, and the solution was frozen in an ice bath. A solid precipitate was collected and dried in a desiccator under reduced pressure. The product was recrystallized once from hexane (filtration). The resulting orange-yellow crystals were washed with several small portions of cold hexane and dried in a desiccator under reduced pressure. The yield was 0.10 g (14%): mp 234–241 °C (lit.¹² mp 239–242 °C); ¹H NMR (60 MHz, CDCl₃) δ 6.77 (s, 4 H), 7.25 (s, 20 H); ¹³C NMR (CS₂, proton decoupled) δ 128.88 (4 C), 129.50 (8 C), 130.35 (4 C), 132.87 (8 C), 134.18 (2 C), 140.89 (2 C), 143.27 (4 C).

Chichibabin's Hydrocarbon ([1,1'-biphenyl]-4,4'-diylbis(diphenylmethyl), 4), a. 4,4'-Bis(diphenylhydroxymethyl)biphenyl (**11**), 4,4'-Dibromobiphenyl (10.9 g, 0.035 mol) was added to 400 mL of refluxing hexane (dried) in a 1-L, 3-necked, round-bottomed flask fitted with a pressure-equalizing dropping funnel, a mechanical stirrer, and a reflux condenser. A nitrogen inlet tube was attached to the condenser, and all subsequent manipulations were carried out under a positive nitrogen pressure.

n-Butyllithium (30.0 mL of a 2.5 M solution in hexane, 0.075 mol) was added to the stirred suspension of the dibromide in hexane. A tan precipitate formed. The reaction mixture was refluxed for 2.5 h. About 13.7 g of benzophenone (0.075 mol) in 50 mL of ether was added over a period of a few minutes, and the mixture was refluxed and stirred for 1.5 h. A green solution was produced, which turned yellow upon exposure to air. The reaction products were poured into a solution containing 200 mL of water and 20 mL of 10% HCl. A yellow solid precipitated and was collected and dried in a vacuum desiccator. The solid was triturated with 75 mL of hot hexane to remove *n*-butyldiphenylcarbinol

and redried in a desiccator. Recrystallization from benzene/hexane (filtration) yielded 6.0 g (33%) of diol **11**: mp 174–175 °C (lit.^{13b} mp 177–178 °C); ¹H NMR (60 MHz, CDCl₃) δ 2.80 (s, 2 H), 7.30–7.47 (28 H).

b. 4,4'-Bis(diphenylchloromethyl)biphenyl (**12**). Dichloride **10** was prepared by treating diol **11** with gaseous HCl following essentially the methods of Schlenk¹² and Vaughan^{13b} (47%): mp 215–219 °C (lit.^{13b} mp 223–225 °C); ¹H NMR (60 MHz, CDCl₃) δ 7.28 (s, 28 H).

c. Dechlorination of Dichloride 12. Dichloride **12** (0.4035 g, 7.236×10^{-4} mol) and mercury (5.8402 g, 2.912×10^{-2} mol) were placed in a Schlenk tube with a break-seal sidearm. The tube was evacuated to about 5×10^{-4} torr, and 5 mL of dry, degassed benzene were vacuum transferred into the system. The ampoule was sealed and shaken for 2 days at room temperature. An intense, blue-violet color developed. The break-seal sidearm was attached to a double Schlenk assembly with a medium porosity fritted disc. The assembly was evacuated on a vacuum line, and the seal was broken. Approximately 5 mL of dry, degassed hexane was transferred into the benzene solution containing Chichibabin's hydrocarbon over a 1-h period. The isolated Schlenk assembly was allowed to stand overnight; crystals had formed by morning. The mixed solvent was removed by filtration and transferred out of the system. All subsequent handling of hydrocarbon **4** was carried out in a drybox. Most of the hydrocarbon isolated consisted of shiny, metallic green crystals, although some violet powder was produced. In all, 0.222 g (63%) of **4** was isolated. The mounting of the X-ray single crystal took place in a dry-nitrogen atmosphere in a dry bag.

UV Study of Chichibabin's Hydrocarbon. All sample preparations were performed in a drybox. Reagent grade benzene (dried) was thoroughly degassed on a vacuum line at about 5×10^{-4} torr. Volumetric flasks were tightly stoppered by using silicone-greased stoppers to prevent solvent evaporation inside the drybox. A 3.63×10^{-3} M solution was prepared in a 100-mL volumetric flask by completely dissolving 0.176 g (3.63×10^{-4} mol) of the crystalline hydrocarbon **4** in benzene. The crystals were first crushed to a powder, and the solution was stirred for 2 days with a magnetic stirrer. A series of concentrations ranging from about 4×10^{-3} – 4×10^{-6} M was made by diluting the 3.63×10^{-3} M solution. Absorbance measurements were performed on a Perkin Elmer 300 spectrometer with the slits set at 2 nm. Quartz cells (0.01 cm) fitted with air-tight Teflon stoppers were employed. All measurements were made immediately, since oxygen leaked slowly into the cells. The concentrations and their measured absorbances were ($\lambda = 310$ and 574 nm, respectively): 3.63×10^{-3} (0.718, --), 2.90×10^{-3} (0.571, --), 2.47×10^{-3} (0.477, 2.902), 2.18×10^{-3} (0.429, 2.577), 1.82×10^{-3} (0.332, 2.036), 7.26×10^{-4} (0.135, 0.828), 9.08×10^{-5} (--, 0.105), and 3.63×10^{-6} M (--, 0.005).

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Registry No. **3**, 26392-12-1; **4**, 6418-52-6.

Supplementary Material Available: Anisotropic thermal parameters for Thiele's hydrocarbon; atomic positional and thermal parameters for Chichibabin's hydrocarbon at -50 and 20°C (5 pages). Ordering information is given on any current masthead. Complete structure reports for Thiele's hydrocarbon (Report No. 83204) and Chichibabin's hydrocarbon at -159°C (84403), -50°C (84404), and 20°C (84405) are available by writing the Molecular Structure Center, Department of Chemistry, Indiana University, Bloomington, IN 47405. The reports contain among other things, complete crystal and diffractometer data, tables of atomic positional and thermal parameters, bond distances and angles, listings of F_o and F_c , and a variety of stereodiagrams.

(51) Activated by stirring with 2 M HCl for a few minutes, washing with deionized water, washing with reagent grade acetone, and drying for 1.5 h.