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Synthesis and Properties of Cycloocta[def]biphenylene, a Stable Benzenoid Paratropic Hydrocarbon^{1,2}

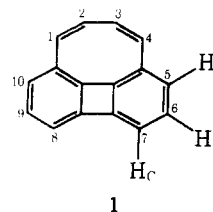
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Abstract: The synthesis and properties of cycloocta[def]biphenylene are described. This hydrocarbon is predicted by conventional models to have simultaneously olefinic, aromatic, and antiaromatic properties. Experiments confirm these predictions. The resolution of this apparent contradiction is discussed.

Aromaticity has played a central role in the development of the theory of chemical bonding.³ The archetypal extremes of behavior, benzene and cyclobutadiene, are now both known.⁴ The elegant studies of the annulenes⁵ and related ring structures⁶ have highlighted the differences between $4n$ and $4n + 2$ ring systems.

The theory of aromaticity has been developed to the point where the chemical and physical properties of new π structures can be predicted with fair confidence.³ An important concept that has emerged from the theoretical investigations is the trilogy of aromatic, olefinic, and antiaromatic classes;⁷ much of the current interest in π systems is with molecules that lie on or near the borders of this classification scheme. This paper, describing in more detail results we have presented earlier,¹ is concerned with the particular molecule cycloocta[def]biphenylene (**1**) which according to



the present classification criteria has the intriguing property of falling simultaneously into all three categories. This paper describes the synthesis of **1**, its chemical and physical properties, and concludes with a discussion of the limitations of the current classification methods.

According to simple HMO theory, molecules containing fused $4n$ rings are predicted⁸ to have substantial delocalization energy and naively might have been expected to possess

some of the special stability found in benzenoid aromatic networks. Despite the considerable effort that has gone into their synthesis, the fused $4n$ ring systems have proved either to be inaccessible or disappointingly olefinic.⁹ Thus, for example, various derivatives of the fused 4–8 network bicyclo[6.2.0]decapentaene were found to be highly reactive and without special stability. More sophisticated calculations that invoke specific electron-repulsion terms and take into account the distance dependence of neighboring resonance integrals, as well as the strain of the underlying σ framework, are in accord with this olefinic character.¹⁰ A more direct, if qualitative, insight into the problem is provided by the algebraic structure count method which reveals that the parent 4–4, 4–8 and 8 networks each have a product of the HMO energy levels of unity, characteristic of polyolefins.¹¹ In other words, compared with aromatic hydrocarbons, such fused $4n$ networks, like polyolefins, have orbitals close to zero, and these are capable of interacting so as to lead to strong bond alternations.

One of the basic aims of this study was to investigate molecules that straddled the division between aromatic and antiaromatic behavior. Since the simple fused $4n$ -ring systems were apparently olefinic, it seemed logical to retain this basic structural element and to add benzenoid rings in such a way as to increase the algebraic structure count (ASC),^{11a} i.e., the number of Kekulé structures taking into account their parity. The phrase "in such a way" is used here, because one of the lessons of the previous theoretical study of such systems revealed that arbitrary addition of benzenoid rings could either increase or decrease the ASC. Previous negative experimental results^{9a,b} illustrate the correctness of this conclusion. Of the many possibilities that appeared reasonably accessible, hydrocarbon **1** looked particularly interesting. It has an ASC of 2 ($\pi_c = 2^2 = 4$). More importantly, the rigidity of the biphenylene subunit combined with the geometry and dimensions of the cyclobutadiene ring almost surely would constrain the hydrocarbon to be planar. Synthesis of **1** thus promised to provide the first example of a hydrocarbon containing a planar cyclooctatetraene ring which would permit whatever antiaromatic contributions it might make to be displayed fully. The choice of **1** was justified by the subsequent calculation of its properties by more refined MO methods as described below.

Calculated Properties of Cycloocta[def]biphenylene. The bond lengths for hydrocarbon **1** were predicted by the SCF model of Lo and Whitehead¹² and are recorded in the right-hand column of Table I. The model, parameterized against ethylene and benzene, includes the effects of σ strain in its empirical bond order–bond length relationship. For comparison, the same SCF model calculations were carried out for biphenylene and butadiene; the predicted and observed bond lengths are recorded in the central columns of Table I. To a first approximation, the predicted structure of **1** is simply the sum of structures of biphenylene and butadiene. Closer examination reveals a tendency of the alternating bonds of the central 8–4 ring network to equalize. In keeping with this tendency, the A and D bonds (see Diagram I) joining the allylic fragments are longer in **1** than in biphenylene, and bonds B and C are more nearly equal. All of these predicted changes are small and within the uncertainty of most X-ray determinations of structure. Similar calculations using the Dewar–deLlano SCF model^{10a} give bond lengths that agree with the Lo and Whitehead values within an average deviation of 0.004 Å.

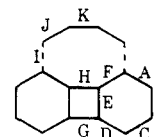
The Lo and Whitehead model yields a resonance energy for **1** of 131.1 kcal/mol compared with 104.9 kcal/mol for biphenylene and 8.7 kcal/mol for butadiene. Thus it would appear that there is a significant stabilizing interaction be-

Table I. SCF Hückel Calculations for Biphenylene, Butadiene, and Cycloocta[def]biphenylene

Bond ^a	Bond length		Bond length Pred ^b
	Pred ^b	Obsd ^c	
Biphenylene			
A	1.414	1.423	1.417
B	1.390	1.385	1.389
C	1.414	1.423	1.413
D	1.390	1.372	1.391
E	1.418	1.426	1.416
F	1.390	1.372	1.395
G	1.484	1.514	1.484
H	1.484	1.514	1.487
Butadiene			
I			1.471
J	1.338	1.344	1.346
K	1.471	1.467	1.471

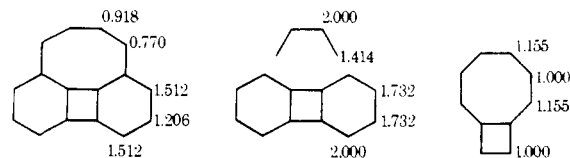
^a See Diagram I. ^b SCF, Lo and Whitehead parameterization. ^c Reference 13.

Diagram I. Cycloocta[def]biphenylene Visualized as the Interaction between Biphenylene and Butadiene



tween the butadiene and biphenylene fragments ($131.1 - 104.9 - 8.7 = 17.5$ kcal/mol) in spite of the marked bond alternation. This energy difference, of course, represents an absolute stabilization. Alternatively, one might ask how much stabilizing interaction is present relative to the interaction found, e.g., in joining a butadiene fragment to two benzenes to give 1,4-diphenylbutadiene. Using the same Lo and Whitehead model gives 17.8 kcal/mol for this latter interaction. With the Dewar–deLlano model, the "Dewar" resonance energy of **1** is 29.0 kcal/mol compared with 30.9 kcal/mol for biphenylene and 0.8 kcal/mol for butadiene for a small destabilization of 2.7 kcal/mol. Thus the two SCF models agree in predicting that the fusion of butadiene to biphenylene to give **1** involves little change in thermodynamic stability, either positive or negative. This is consistent with the bond lengths calculated for the eight-membered ring of **1**. Viewed as a whole, however, hydrocarbon **1** possesses considerable resonance energy and would be classified as aromatic in either the classical or "Dewar" sense.

The implication of the foregoing discussion is that hydrocarbon **1** probably should prove to be quite reactive in spite of the large delocalization energy. A convincing demonstration of this point is provided by examining the Dewar reactivity numbers³ for **1** and for the closely related structural fragments given below. Two conclusions can be drawn. The



first is that electrophilic reaction of **1** should occur more rapidly than reaction of even butadiene or the parent bicyclo[6.2.0]decapentaene. The second, and related conclusion, is that this high reactivity is a property related to the entire π network and not just a fragment of it.

An equivalent way of predicting the high reactivity of **1** is by way of a simple Hückel calculation which gives a smaller HOMO–LUMO separation for **1** (1.00β) than for biphe-

nylene (1.24 β). The smaller separation is consistent with the smaller ASC value of **1**.

One caveat is that the Dewar reactivity numbers are based on an equal bond-length model. Introduction of bond alternation would cause the localization energies to move toward the values for the butadiene and biphenylene fragments.

Thus far the calculations have suggested that hydrocarbon **1** possesses both aromatic (thermodynamic stability) and olefinic (reactivity) properties. This contradiction is not disturbing since it is the result found theoretically and experimentally for many polycyclic benzenoid hydrocarbons (e.g., phenanthrene) and merely reflects the bane of all categorizations; the only true benzenoid hydrocarbon is benzene itself.

A more startling prediction for **1** is its ring current. Using the McWeeny ring current model¹⁴ with iterated Hückel MO's (close to the SCF bond orders calculated above), it is found that the four- and eight-membered rings give large paramagnetic currents (-0.63 and -0.56 , respectively, benzene $\equiv +1.00$), while the benzene rings show markedly reduced diamagnetic currents ($+0.47$). For comparison, biphenylene using the same procedure gives a calculated paramagnetic current in the four-membered ring of -0.66 and diminished diamagnetic currents in the benzene rings of $+0.65$. Figeys,¹⁵ on the basis of a similar calculation, has quantitatively ascribed to these opposing ring currents the observed upfield shifts of 0.47 and 0.57 ppm of biphenylene relative to benzene. On the basis of the presently calculated currents and the Waugh and Fessenden ring-current model,¹⁶ hydrocarbon **1** should show even larger upfield shifts (ca. 0.5–1.0 ppm). If the calculations were taken literally, hydrocarbon **1** could be said to possess a net *paramagnetic* ring current, and by that criteria would be classified as an *antiaromatic* species.

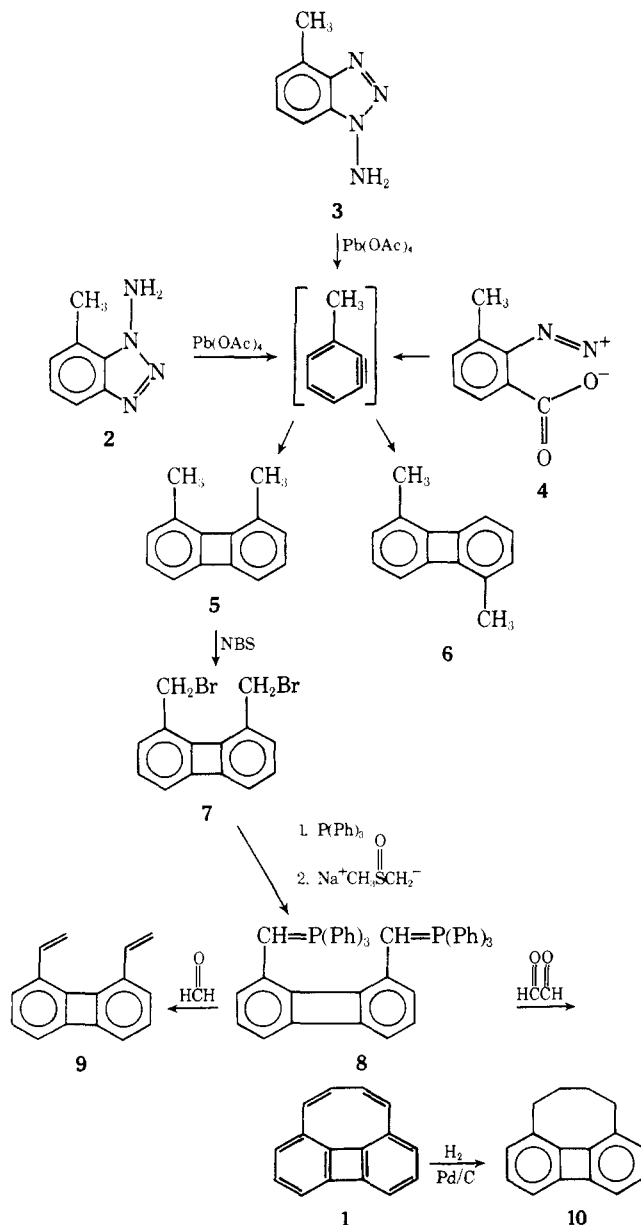
The model calculations thus lead to the amusing contradiction that hydrocarbon **1** is at once aromatic, olefinic, and antiaromatic depending on one's criteria. If the molecule seemed worth synthesizing before the calculations, it became a necessity afterward. A final calculation which, although simple, proved invaluable in the realization of **1** was to note from the Streitwieser^{3c} empirical correlation of spectra with the HOMO–LUMO separations that **1** should have a visible absorption near 540 nm. This is probably low since biphenylene is calculated to absorb at 364 nm (obsd, 395 nm).

These calculations help characterize the target compound to be a dark-colored (probably red) hydrocarbon, thermally stable but reactive toward electrophilic reagents, and possessing an NMR showing significant upfield shifts in both the aromatic and olefinic regions.

Synthesis and Characterization of 1. There are several paths that could lead to **1**; however, because of the known difficulties in forming biphenylene,¹⁷ it seemed better to form the biphenylene skeleton early in the sequence. The subsequent building of the four-carbon bridge could in principle be accomplished by attaching an appropriate chain to the 1 position and then closing the ring to the 8 position. Several such attempts failed,¹⁸ and we turned to the alternative of starting with substituents in the 1 and 8 positions of biphenylene and joining them. This led to the exploration of 1,8-dimethylbiphenylene as a precursor.

1,8-Dimethylbiphenylene can be made either by the thermal decomposition of the diazocarboxylate **4** prepared from 2-amino-3-methylbenzoic acid, using the method of Friedman,¹⁹ or by the lead tetraacetate oxidation of 1-amino-7 (or 4)-methylbenzotriazole (**2** or **3**), using the method of Campbell and Rees.²⁰ The first method has the advantage that 2-amino-3-methylbenzoic acid is commercially avail-

able, but the yield is low, and it presents an explosion hazard on a large scale. The lead tetraacetate method requires several steps to obtain 1-amino-7-methylbenzotriazole, but it is apparently safe and gives an unusually high yield for a yield for a benzyne dimerization. For these latter reasons, we chose this route.²¹ We confirmed the high yield²² of 1,5- and 1,8-dimethylbiphenylene and consistently obtained a ratio of 45 to 55%, respectively, for the isomers²³ ($\pm 3\%$). Changing the solvent from methylene chloride to benzene had no effect on the ratio. Also changing the scale of the reaction had no effect. Nor did the use of 1-amino-4-methylbenzotriazole (**3**)²⁴ or the diazocarboxylate as precursors have any effect.



The mixture of 1,8- and 1,5-dimethylbiphenylenes could be separated easily by ethylene glycol codistillation on a spinning-band column. The isomers, which had almost identical ir and NMR spectra, were identified by their relative dipole moments. The less volatile isomer was found to have a dipole moment of 0.64 D which is close to what would be expected of 1,8-dimethylbiphenylene if it is regarded simply as the sum of two toluenes.

1,8-Dimethylbiphenylene was converted into the title compound **1** through the series of steps shown above. The first step was the reaction with NBS to give the dibromide **7**

Table II. NMR Data for Representative Biphenylenes^a

Compd	Chemical shift, τ			Coupling constant, Hz		
	H _A ^b	H _B ^b	H _C ^b	J _{AB}	J _{BC}	J _{AC}
Biphenylene	3.4	3.4	3.3	8.3	7.0	0.84
5	3.56	3.44	3.63	8.3	6.8	0.75
6	3.57	3.43	3.63	8.5	6.7	0.66
9	3.13	3.30	3.42	8.4	6.9	0.74
1	4.22	3.83	4.00	8.2	6.9	0.60

^a NMR spectra were taken at 60 MHz using carbon tetrachloride as solvent and Me₄Si as reference. The spectra were analyzed using a LAOCOON3 computer program. ^b See structure 1 for nomenclature.

followed by a reaction with triphenylphosphine to give the bisphosphonium salt. This was converted with base (either *n*-butyllithium in THF or better with dimsyl sodium in DMSO) to the bisylid **8**. Treatment of the bisylid with a solution of freshly prepared glyoxal monomer gave a complex mixture of products from which the desired hydrocarbon, a dark-red solid, could be isolated by column chromatography in 12% yield.

The identity of **1** was established in the following manner. High resolution mass spectrometry gave a parent peak of *m/e* 202.0778 (calcd for C₁₆H₁₀, 202.0785) with isotopic peaks at 203 and 204 of appropriate magnitude. As would be expected for a hydrocarbon with a low ionization potential, the 202 parent peak was the largest in the spectrum. Supportive evidence was provided by the appearance of a strong dication P/2 peak at 101.0392 (calcd for 1/2 C₁₆H₁₀, 101.0393) and a (P + 1)/2 isotope peak at 101.5409 (calcd 101.5409). From the magnitude of the (P + 1)/2 peak, it appeared that the P/2 peak contained little contribution from a C₈H₅ monocationic fragment.

The NMR spectrum of **1** in CCl₄ showed two groups of peaks in the ratio of 6:4 assignable to the aromatic and olefinic protons, respectively. The aromatic proton absorptions gave a complex ABC pattern with chemical shifts of τ 4.22, 3.83, and 4.00 and coupling constants of $J_{AB} = 8.2$, $J_{AC} = 0.6$, and $J_{BC} = 6.9$ Hz. Although the A and C protons cannot be distinguished by this evidence, proton B is unique. Interestingly it absorbs closest to the normal aromatic region (ca. τ 2.8), as would be expected for the proton furthest from the anticipated paramagnetic ring currents of the four- and eight-membered rings. It should be emphasized, however, that all three aromatic absorptions are shifted upfield and, as shown in Table II, by an amount that is approximately twice the upfield of biphenylene itself. Figure 1 shows the amplified downfield portion of the spectrum along with the simulated spectrum using the constants given above.

The observed coupling constants are in good agreement with those calculated by the empirical correlation of Günther et al.²⁵ against SCF bond orders. Thus using our SCF bond orders, we calculate 8.1 Hz for J_{AB} and 6.9 Hz for J_{BC} . The relative constancy of the coupling constants indicates no major geometric distortions have occurred in passing from biphenylene to **1** and supports the idea that **1** is best thought of as butadiene attached to biphenylene.

The olefinic protons give rise to a closely spaced doublet at τ 5.37 and 5.40. In divinylbiphenylene, the olefinic protons absorb with an ABC pattern. The proton nearest to the benzene ring (the A proton) absorbs at τ 3.36 reflecting the inductive and diamagnetic influence of the nearby benzene ring. The B proton absorbs at τ 4.68. Thus relative to divinylbiphenylene, it is clear that the protons at C₁ and C₄ in **1** are displaced upfield by about 2.0 ppm, while the protons at C₂ and C₃ in **1** are displaced upfield by about 1.0–1.3 ppm. The larger upfield shift of the C₁–C₄ protons relative to di-

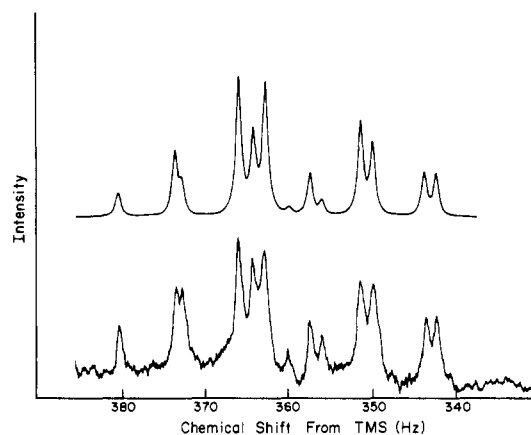


Figure 1.

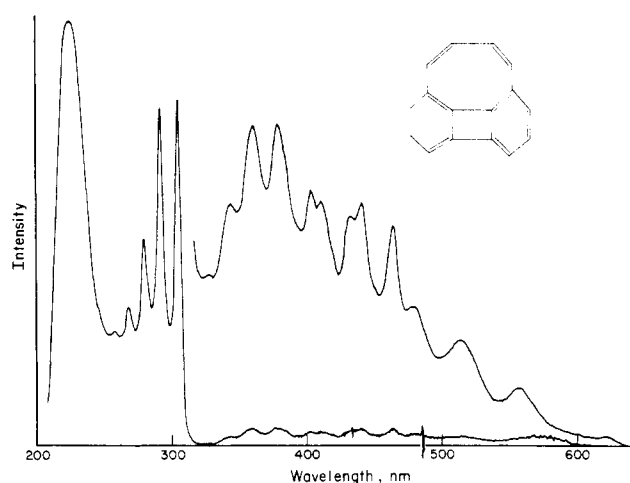


Figure 2.

vinylbiphenylene can be ascribed in part to the slightly diminished diamagnetic currents in the benzene rings and in part to a downfield shift of the C₂–C₃ protons by the inductive effect of the additional sp² center in **1**. The near coincidence of the olefinic absorptions of **1** is by this interpretation accidental. Still larger shifts are found if dibenzo-[*a,c*]cyclooctatetraene is used as a reference [τ 2.82 (8 H), 3.35 (2 H), 4.00 (2 H)].²⁶

Additional evidence in favor of the assigned structure is that hydrogenation of **1** gave a yellow C₁₆H₁₄ hydrocarbon (*m/e* 206) with NMR absorptions having chemical shifts characteristic of an alkylated biphenylene: τ 3.3–3.8 (6 H, ABC), 7.5 (4 H, m), and 8.3 (4 H, m).

The uv-visible spectrum of **1** is reproduced in Figure 2; the absorption bands together with those for biphenylene and 1,8-divinylbiphenylene are collected in Table III. At least three major band systems can be discerned. In either cyclohexane or methanol, the longest wavelength absorption starts with a low intensity at 621 nm ($\log \epsilon$ 2.91 at 327 nm). At 305 nm, a new band system takes over ($\log \epsilon$ 4.31), and it also is followed by a series of vibrational steps of gradually decreasing intensity ($\log \epsilon$ 2.86 at 258 nm). Finally, there is an intense band at 225 nm ($\log \epsilon$ 4.35).

The analysis of the electronic spectrum is still in progress, but it would appear that the three bands observed are related to the three bands of biphenylene at 395 nm ($\log \epsilon$ 2.0), 400 (3.8), and 250 (4.9). The long wavelength band of biphenylene is strictly forbidden by symmetry. The most probable origin of the 621-nm band is a coupling of the long-axis biphenylene band (395 nm) with the long-axis

Table III. Uv-Visible Data for Representative Biphenylenes^a

Biphenylene		1,8-Divinyl-biphenylene		Cycloocta[def]-biphenylene	
Wave-length, nm	Log ϵ	Wave-length, nm	Log ϵ	Wave-length, nm	Log ϵ
241	4.60	234	4.47	225	4.35
250	4.90	273	4.54	258	3.86
340	3.63	280	4.59	268	3.94
345	3.59	363	3.58	280	4.10
360	3.80	380	3.75	292	4.30
		400	3.67	305	4.31
				327	2.91
				342	3.05
				360	3.17
				378	3.17
				402	3.07
				410	3.05
				431	3.02
				440	3.05
				463	3.00
				478	2.81
				512	2.69
				557	2.42
				621	1.63

^a Uv-visible spectra were taken on a Cary 14 spectrometer using Fisher spectranalyzed cyclohexane as the solvent.

transition of *cis*-butadiene (ca. 215 nm) to give a nearly forbidden out-of-phase combination.²⁷

In summary, the observed behavior of **1** is close to that predicted by the various models.²⁸ It is a dark-red hydrocarbon with quite long-wavelength absorption. The NMR shows a marked paramagnetic NMR shift indicative of the planar $4n$ π networks but, in spite of the presence of these "antiaromatic" rings, the compound is thermally stable. Preliminary evidence also indicates a high reactivity toward electrophiles.²⁹ Thus it appears that **1** does indeed fall simultaneously into all three categories of π systems: olefinic, aromatic, and antiaromatic. The remaining task is to resolve this apparent contradiction.

As indicated in the introductory section, high reactivity combined with special thermodynamic stability represents no real dilemma. On the one hand, multiring aromatic molecules are expected to have high reactivities because of their improved possibilities for stabilizing reaction intermediates. Moreover, if the molecule contains a short olefinic unit joined with an aromatic one (as the calculations suggest for **1**), both high reactivity and stability are to be expected.

The significant question is why these structural units give paramagnetic ring currents. The answer to that question can be found in the ring-current model of McWeeny¹⁴ and the results of Pople and Untch.³⁰ An induced diamagnetic ring current (i.e., a rise in energy) is the normal response of a molecular orbital to an applied magnetic field but, as Longuet-Higgins pointed out,³¹ when there are occupied and unoccupied energy levels that mix strongly under the influence of the field, a net lowering of the energy (paramagnetism) can occur. This is clearly very significant for molecules with degenerate levels like cyclobutadiene and planar cyclooctatetraene, but it persists when the levels are merely close. This is precisely the situation for molecules with small ASC values such as **1**. A small ASC value, however, is not a sufficient condition. In terms of the McWeeny perturbation treatment, another factor that controls the magnitude of the magnetic response for a given ring ($4n$ or $4n + 2$) is the area of the ring times the product of the resonance integrals around the bonds of the ring. Acyclic olefins (which are ring compounds where one of the resonance integrals has gone to zero) have no ring current. Rings in which bond alternation occurs will still give ring currents, because

the diminution of the resonance integrals for the long bonds is largely compensated for by the increase in the integrals for the short ones. Thus a Kekulé structure for benzene with alternating long and short bonds (by the usual convention a nonaromatic species) gives a calculated ring current of about 0.5 of the value for benzene itself, the exact value being determined by the choice of distance dependence for the resonance integral. The ring currents of large rings (large currents because of the large area) are more sensitive to bond alternation because of the greater number of integrals entering the product. These points are all well illustrated by the calculations of Pople and Untch.

From this discussion, it is apparent that the source of the conflicting evidence for **1** lies with the faulty assumption that sign alone of the ring current is a measure of aromaticity. Thus, for example, a paramagnetic response reveals only the presence of a ring containing $4n$ vertices and says nothing about whether its bonds are equal or alternating. To be a measure of aromaticity, one would have to define a magnetic response for each size of ring in both its equal bond-length and alternating bond-length forms and to inquire where on this scale the actual response came.

The net paramagnetic response of $4n$ -membered rings is calculated to be much larger than the diamagnetic responses of $(4n + 2)$ -membered rings. In **1**, the paramagnetic contributions of the four- and eight-membered rings dominate the diamagnetic contributions of the two six-membered rings in spite of the strong bond alternation of the former. This situation has been obscured with previous eight-membered ring species, because their nonplanarity led to very small bond integrals and hence small ring currents. By use of the ASC method to identify promising molecules, it should be possible to devise a set that would show a range of diamagnetic and paramagnetic responses. Their synthesis and measured magnetic properties could make ring currents a useful quantitative measure of bond alternation.

Experimental Section

Separation of 1,5- and 1,8-Dimethylbiphenylene. 1-Amino-7-methylbenzotriazole was converted into a mixture of 1,5- and 1,8-dimethylbiphenylenes using the method of Campbell and Rees.²⁰ The mixture of isomers was separated by codistillation with ethylene glycol on a 10 mm \times 36 in. spinning-band column and monitored by GLC (5 ft, 5% SE30 at 150°); fractions greater than 90% purity were combined. Each of the partially purified isomers was heated with fresh ethylene glycol (75 ml/g of dimethylbiphenylene) with stirring until the dimethylbiphenylene melted. The mixture was cooled slowly, with stirring, to -15° . The solid that separated was collected and washed with three portions of cold methanol. This gave the 1,5 and 1,8 isomers of dimethylbiphenylene in about 98% purity. The isomers after separation by codistillation could be purified further by recrystallization from methanol.

Determination of the Dipole Moments of 1,5- and 1,8-Dimethylbiphenylene. The dipole moments (Table IV) were determined by the method of Halverstadt and Kumler.³²

The dielectric constants were measured with a WTDFL 1-heterodyne beat apparatus (2.0 Mc) at 25.0°. Cyclohexane (Fisher spectranalyzed, passed through a column of 4A molecular sieve pellets immediately before use) was used as the solvent. Its dielectric constant was taken as 2.0148. The compound with the smaller polarizability was taken as 1,5-dimethylbiphenylene, and then its total polarizability was used as a much better value for the sum of the atomic and electronic polarizabilities of the 1,8 isomer. This resulted in a value of 0.64 D for the dipole moment of 1,8-dimethylbiphenylene.

Bromination of 1,8-Dimethylbiphenylene (7). A mixture of 1,8-dimethylbiphenylene (5 g), *N*-bromosuccinimide (11 g, recrystallized from water and dried over phosphorus pentoxide for at least 4 hr at 0.15 mmHg), benzoyl peroxide (0.5 g), and carbon tetrachloride (125 ml, Fisher spectrograde) was refluxed for 30 min. If the reaction did not start within this amount of time, more benzoyl peroxide was added, and the reaction mixture was refluxed for an

Table IV. Dipole Moment Data

	α	β	P_2	Estimated Pa + Pe ³³	μ
Biphenylene	0.485	-0.365	53.4	53.4	0
1,5-Dimethyl- biphenylene	0.457	-0.378	60.8	62.5	-0.28
1,8-Dimethyl- biphenylene	0.651	-0.378	69.8	62.5	-0.59

additional 30 min after the reaction started. The hot mixture was filtered and most of the solvent removed. Addition of a small amount of petroleum ether induced crystallization, and the product was collected and washed with another portion of petroleum ether. The crude yield varied from 60 to 80%; mp 150–185° dec; NMR (CDCl₃) τ 3.2–3.5 (3 H, m), 5.51 (2 H, s). It was difficult to purify and decomposed on a silica gel column.

α,α' -Bis(triphenylphosphonio)-1,8-dimethylbiphenylene Dibromide. A mixture of the crude dibromide (2 g), triphenylphosphine (3.5 g, Aldrich), and dry DMF (50 ml) was heated on a steam bath in a wide-mouthed flask fitted with a drying tube. After 15 min, the phosphonium salt began to precipitate and after a total of 4 hr, the mixture was cooled to room temperature and the product collected. It was washed with a mixture of benzene and DMF (3:1) followed by dry ether. It was dried over phosphorus pentoxide at 20 mmHg overnight to yield 4.4 g (85%) of the bisphosphonium salt.

Purification of Glyoxal. Glyoxal trimer (11 g, MC&B) and phosphorus pentoxide (8 g) were placed in a 125-ml flask and distilled with a direct flame through a piece of glass tubing into another flask kept at -78°. The monomer was placed under vacuum (25 mm) to remove most of the formaldehyde and then distilled bulb-to-bulb at 1 mmHg with the receiver cooled to -78°. Dry ether or THF (90 ml) was added, and the solution was redistilled bulb-to-bulb to give a relatively stable solution of glyoxal monomer.

Cycloocta[def]biphenylene (1). Using *n*-Butyllithium in THF. The bisphosphonium salt (6.4 g) was suspended in dry THF (500 ml) under a nitrogen atmosphere. The mixture was cooled to 0°, and the stoichiometric amount of *n*-butyllithium was added. The mixture turned a dark blood-red color. It was stirred for 1 hr at 0°, and then the stoichiometric amount of glyoxal in THF was added dropwise over a period of 1 hr. After stirring for 2 more hr, ca. 0.3 equiv of glyoxal was added, and then the mixture was warmed to about 45° for 30 min before work-up.

The mixture was filtered and most of the THF removed and replaced by ether. The mixture was then washed twice with water, the ether layer dried (K₂CO₃), and the solvent removed. Chromatography on silica gel with petroleum ether gave a red fraction which contained about 15 mg (1% yield) of 1. It was purified by preparative GLC (2 ft, 5% SE30 170°) followed by chromatography on alumina with petroleum ether leaving 7 mg of product, mp 99–100°.

The spectral data for 1 were consistent in all respects with the assigned structure: high-resolution mass spectrum *m/e* 202.0778, 101.0392, and 101.5409; NMR (CCl₄) τ 3.6–4.4 (3 H, ABC), 5.38 (2 H, d); ir (max) (KBr) 1380, 1260, 1200, 1120, 965, 780, and 720 cm⁻¹ among others.

Cycloocta[def]biphenylene (1). Using Dimsyl Sodium in DMSO. Dimsyl sodium was made from sodium hydride (0.15 g, 57% in oil) and DMSO (500 ml, distilled from CaH₂) by the method of Corey and Chaykovsky.³⁴ The solution was cooled to 40°, and 1.07 g of the bisphosphonium salt (1.07 g) was added. The mixture turned a dark-red color but more slowly than when *n*-butyllithium was used as the base. The bisphosphonium salt slowly dissolved, and the mixture was stirred for a total of 1.25 hr. Then 13 ml of a solution of glyoxal in ether (0.8 g/90 ml ether) was added over a period of 2.25 hr. The temperature was then raised to 50° and the solution stirred for an additional 30 min. The work-up was accomplished by pouring the solution onto 500 ml of ice water and extracting four times with a total of 300 ml of ether. The ether layers were combined, washed three times with water, and dried (K₂CO₃), and the solvent was removed. The product produced in this manner was purer than that produced using *n*-butyllithium, and column chromatography on alumina with petroleum ether was sufficient for

purification. The yield of 1 was 30 mg (12%) and had the same properties as that produced using *n*-butyllithium.

1,8-Divinylbiphenylene (9). The bisylid was prepared as before using 2 g of the bisphosphonium salt, 0.3 g of 57% NaH, and 500 ml of dry DMSO. Formaldehyde was bubbled through the solution until the color turned from dark red to light yellow. The solution was then warmed to 50° for 15 min. Work-up was as before and gave 0.44 g of 9 (quantitative yield); mp 104–106°; NMR τ 3.0–3.6 (2 H, ABC), 4.2–4.8 (1 H, ABC); ir (max) (KBr) 1380, 1240, 988, 970, 907, 780, and 720 cm⁻¹ among others.

Hydrogenation of Cycloocta[def]biphenylene to Give 10. Palladium on charcoal³⁵ (5 mg), cycloocta[def]biphenylene (20 mg), and absolute ethanol (10 ml) were placed in a flask. The flask was flushed with nitrogen followed by hydrogen and the flask sealed with a ground-glass stopper and covered with Parafilm. The mixture was stirred for 24 hr. Purification of the tetrahydrocycloocta[def]biphenylene (10) was accomplished by column chromatography on alumina with petroleum ether followed by GLC (2 ft, 5% SE30, 160–): mp 78–80°; NMR (in CCl₄) τ 3.3–3.8 (6 H, ABC), 7.5 (4 H, M), 8.3 (4 H, M); mass spectrum *m/e* (rel intensity) 206 (100), 189 (12.1), 178 (23.1), 165 (10.6), 152 (6.5).

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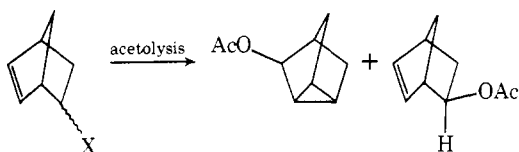
Stable Carbocations. CLXXVI.^{1a} 3-Nortricyclyl Cations. Question of Charge Delocalization in Rigid Cyclopropylcarbiny Systems^{1b}

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Abstract: A series of 3-nortricyclyl cations 1-R (R = H, CH₃, CH₂CH₃, OH, C₆H₅, Cl and F) have been prepared under stable ion conditions and characterized by proton and carbon-13 NMR spectroscopy. NMR data indicate that both secondary and tertiary 3-nortricyclyl cations are classical carbenium ion with charge delocalization into the cyclopropyl ring. Steric factors and molecular rigidity of carbocations investigated are of great importance in dealing with the question of the mode of charge delocalization.

Solvolyses of esters of *exo*- and *endo*-2-norbornen-5-ols and 3-nortricyclanol have been of interest since the initial reports of their interconversion and reactivities by Roberts² and Winstein,³ providing one of the key examples for



homoallylic cations.⁴ Strained δ bonds can provide very strong participation into transition states of solvolysis reactions.⁵ Such interaction is particularly noticed in carbocations.⁶ Among neighboring groups which are able to provide stabilization to adjacent carbocationic center, the effectiveness of the cyclopropyl group is well documented.⁷ The interaction between strained cyclopropane δ bonds and the adjacent empty or developing p orbital is shown to reach its maximum in a bisected geometry,^{6,8} which was confirmed by the direct observation of several long-lived cyclopropylcarbiny cations.⁹

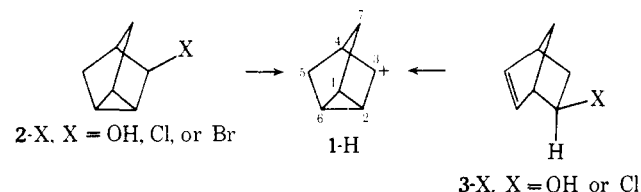
The cyclopropane ring in the geometrically rigid 3-nortricyclyl cations is situated in a favored bisected configuration toward the carbenium ion center for maximum charge delocalization. A preliminary carbon-13 NMR study^{1b} however, showed that charge delocalization is more limited or not as effective as in the corresponding conformationally mobile cyclopropylcarbiny cations.⁹ Steric factors and rigidity in the studied system are therefore of great importance in dealing with the question of charge delocalization in carbocations. We have discussed extensively in our preceding work the question of δ bond delocalization in carbocations via two-electron, three-centered bond formation.¹⁰ We also expressed our view that the mode of charge delocalization from trivalent carbenium ions to five-coordinated carbonium ions¹¹ is generally a continuous process with

faster electronic movement being followed by slower nuclear reorganization. The extent of such deformation can vary greatly in different systems.

Although homoallylic participation¹² in the solvolysis of dehydronorbornyl-nortricyclyl type systems had received considerable attention in recent years,¹³ the intermediate ions involved in the reactions have yet not been satisfactorily identified. The involvement of both unsymmetrical dehydronorbornyl (or norbornenyl) cations and symmetrical nortricyclyl cations had been discussed in an attempt to rationalize the overall product distribution in the solvolysis of these derivatives. In our preliminary studies, we have shown^{1b} that the directly observed 3-nortricyclyl cations under stable ion conditions are symmetrically charge-delocalized, classical ions. We now wish to report in full our comprehensive investigation of the parent, as well as alkyl-, aryl-, and halogen-substituted 3-nortricyclyl cations.

Results and Discussion

Preparation of 3-Nortricyclyl Cations. The parent, secondary 3-nortricyclyl cation 1-H was generated from 3-nortricyclanol 2-OH, or 3-chloro- or 3-bromonortricyclanes^{13c,h} (2-X, X = Cl or Br) in $\text{SbF}_5\text{-SO}_2\text{ClF}$ solution at -78° . At



tempts to prepare 1-H cleanly from dehydronorbornane derivatives 3-X (X = OH or Cl) were complicated by the complexation between the double bond and SbF_5 and consequently resulted in side reactions. Quenching solutions of ion 1-H at -78° with potassium carbonate buffered ice-