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(13) In order to ensure that the protonations described in the text reflect equilibrium (rather than kinetic) effects, in each case where an acid HA was observed *not* to reconvert **13** to **7**, we demonstrated independently that its conjugate base A^- did in fact convert 7 to **13**.

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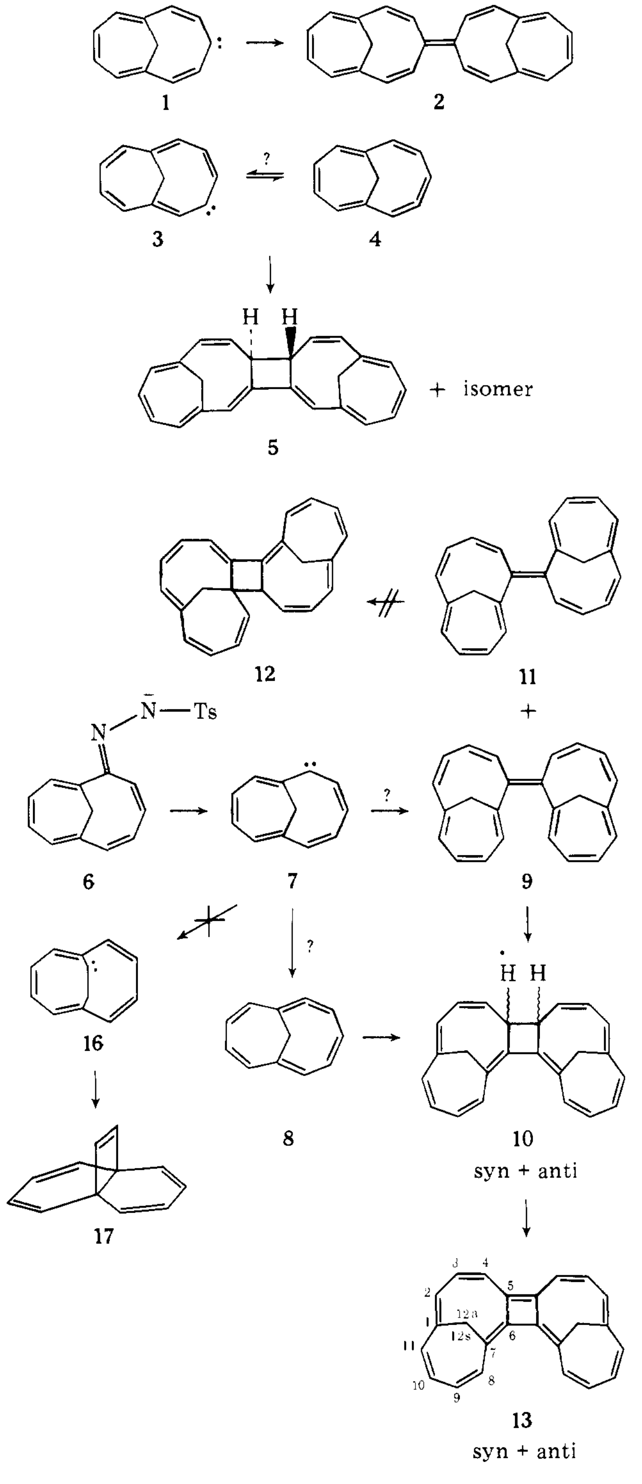
Bridged 22π Annulenes from 6,11-Methano[11]annulenylidene

Sir:

We have recently reported the generation and some of the chemical properties of **1**[1,2,5,6] and **3**,[3-6] two of the five possible methano[11]annulenylidenes in which the vacant orbital of the carbene may be an integral component of a carbocyclic aromatic π-system. At this time, we report the synthesis and pyrolysis products of the tosylhydrazone sodium salt **6**, a reaction which should give a third isomeric methano[11]annulenylidene **7**. This carbene was of particular interest because, in contrast to **1** and **3**, the proximity of the methano bridge in **7** introduces the possibility of a carbene-carbene rearrangement to **16**, a carbene that would be expected to undergo facile hydrogen migration to give the known [4.4.2]propellane **17**.[7] In fact, as in the case of **1** and **3**, in the absence of substrates the presumed carbene from **6** gave only products believed to originate from carbene (or allene) dimers; no **17** was detected. However, the dimers from **7** were found to be exceptional in that the probable intermediates (**10**) spontaneously lose hydrogen to give the totally unsaturated hydrocarbons **13** (syn and anti). To the best of our knowledge, these are the first recorded bridged [22]π annulenes.[8] *syn-* and *anti-* **13** show the further remarkable characteristic of existing in the unexpected localized forms shown.



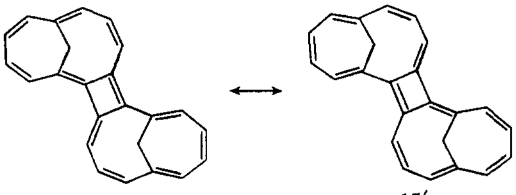
The ketone[9] required for preparing **6** was synthesized from 2-bromo-1,6-methano[10]annulene[10] in two steps (1.5% overall yield) by the method developed by Vogel.[11] Conversion to the tosylhydrazone (~55%) (mp (CH_3OH/hexane 2:1) 106-108 °C; NMR $\delta(CDCl_3)$ 8.05-5.36 (12 H, m), 4.28 (1 H, part of AB system, $J = 11.5$ Hz), 2.35 (3 H, s), 1.20 (1 H, part of AB system, $J = 11.5$ Hz), N-H varies; high resolution MS (calcd 338.1088, found 338.1089)) was effected by refluxing (2 h) an ethanol solution of the ketone, tosylhydrazide,

Table I. Proton Magnetic Resonance Data[a] for **13**

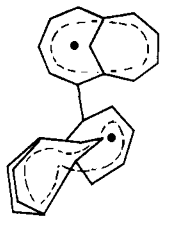
Proton	Chemical shift (δ)	
		Major Isomer of **13**
2	5.76	Broad doublet; $J_{2,3}$ = 5.0 Hz; small long range coupling to H_8 and H_{11}; $J_{2,12s}$ = 1.2 Hz, $J_{2,12a}$ = 0.5 Hz
3	6.59	Doublet of doublets; $J_{2,3}$ = 5.0 Hz; $J_{3,4}$ = 11.6 Hz
4	7.28	Doublet; $J_{3,4}$ = 11.6 Hz
8	6.64	Broadened doublet; $J_{8,9}$ = 13.4 Hz; small long range coupling to H_2
9	5.94	Doublet of doublets; $J_{8,9}$ = 13.4 Hz, $J_{9,10}$ = 7.5 Hz
10	5.57	Doublet of doublets; $J_{9,10}$ = 7.5 Hz, $J_{10,11}$ = 12.3 Hz
11	6.33	Broad doublet; $J_{10,11}$ = 12.3 Hz, small long range coupling to H_2
12s	5.19	Doublet of doublets; $J_{12a,12s}$ = 10.8 Hz, $J_{2,12s}$ = 1.2 Hz
12a	2.79	Broadened doublet; $J_{12a,12s}$ = 10.8 Hz, $J_{2,12a} \cong 0.5$ Hz
		Minor Isomer of **13**
2	6.00	Broad doublet; $J_{2,3}$ = 5.0 Hz, $J_{2,12s}$ = 1.0 Hz, $J_{2,12a}$ = 0.5 Hz
3	6.71	Doublet of doublets, $J_{2,3}$ = 5.0 Hz, $J_{3,4}$ = 11.4 Hz
4	7.43	Doublet; $J_{3,4}$ = 11.4 Hz
8	6.44	Broadened doublet; $J_{8,9}$ = 13.0 Hz
9	6.07	Doublet of doublets; $J_{8,9}$ = 13.0 Hz, $J_{9,10}$ = 7.1 Hz
10	5.76	Doublet of doublets; $J_{9,10}$ = 7.1 Hz, $J_{10,11}$ = 12 Hz
11	6.50	Broad doublet; $J_{10,11}$ = 12.0 Hz, $J_{11,12a} \leq 0.5$ Hz, small long range coupling to H_2
12s	5.21	Doublet of doublets; $J_{12a,12s}$ = 10.7 Hz, $J_{2,12s}$ = 1.0 Hz
12a	2.26	Broadened doublet; $J_{12a,12s}$ = 10.7 Hz, $J_{2,12a} \cong 0.5$ Hz, $J_{11,12a} \leq 0.5$ Hz

[a] Spectra were obtained on a Varian XL-100/15 instrument in $CDCl_3$ solution. Shifts are in ppm referred to internal Me_4Si.

and sulfuric acid in a flask equipped with a Soxhlet extractor in which a thimble was charged with anhydrous $MgSO_4$. The sodium salt was prepared with sodium hydride in the usual way. Pyrolysis of the salt in refluxing diglyme (3-15 min) gave variable yields (42 to ca. 85%) of mixtures consisting primarily of two hydrocarbons (normally in a ratio of ca. 3:1) to which we assign the syn and anti forms of **13**: UV major isomer (dioxane) λ_{max} 251 nm (ϵ 38 800), 368 (7050); minor isomer (dioxane) 251 (74 800), 378 (14 500). These hydrocarbons gave beautiful needles (major isomer, deep orange red mp brown smoke appears at 280 °C, needles dec at 310 °C) and orange red (minor isomer, mp 241-243 °C). Although attempts to obtain an unequivocal structure of the major isomer of **13** by x ray were unsuccessful careful examination of the NMR of the two products leaves little question as to the structures although the stereochemistry remains unknown. The NMR data are given in Table I. As is typical of methanoannulenes, Table I, some of the most telling structural information can be obtained by scrutiny of the resonances of the methano hydrogens.[12] For example, the NMR's of the methano hydrogens of **13** yield the following structural information: (1) Combined with the molecular weight (high resolution MS, calcd 306.1407; found (major isomer) 306.1398, (minor isomer) 306.1398), the presence of signals for only two kinds of methano hydrogens (as well as the simplicity of the rest of the first-order spectrum) requires symmetrical structures. (2) The geminal coupling constants of 10.8 (10.7) Hz exclude cyclopropane (or norcaradiene) structures. (3) From models it is clear that the bridge proton syn to the seven-membered ring (H_{12s}) is more favorably situated for allylic coupling to H_2 than is the proton syn to the eight-membered ring (H_{12a}). From this evidence it is assigned the shift of ca. 5.2 ppm. (4) The low field chemical shift of the hydrogen syn to the seven-membered ring excludes a cycloheptatriene structure, thus requiring bond localization as depicted in **13.** This latter conclusion is confirmed by the coupling constants of vicinal vinyl hydrogens (alternating J = 11.4-13.4 Hz and J = 5.0-7.5 Hz as expected of alternating double and single bonds). Not only do the strongly alternating coupling constants support the localized structures **13** but they exclude structure **15** which is possible but less likely on mechanistic grounds. Thus, in order for the methano hydrogens of the two bicyclic rings in **15** to be equivalent, **15** and **15′** must either be equally contributing resonance forms or the two structures must be in rapid equilibrium. In either event, the coupling constants of the ring hydrogens would not be expected to be strongly alternating.


15 ⟷ 15′

A priori, the chemistry of **7** would be expected to more nearly resemble **1** than **3**.[13] However, formation of **13** (for which **10** is the presumed precursor) from **6** suggests exactly the opposite. To attempt to understand this, scrutiny of the possible origin of the dimethylenecyclobutanes **10** (syn and anti) is informative. These dimers could reasonably originate from either dimerization of the allene **8** or electrocyclic closure of the fulvalenes **9.** Based solely on our earlier work,[4] dimerization of the allene would have to be favored because the stereochemistry of the cyclobutane hydrogens in the dimer resulting from **3** or **4** is wrong for an allowed electrocyclic closure of a fulvalene but is correct for allene dimerization. However, it has recently become increasingly clear that allene dimerization proceeds via a diradical mechanism with free rotation around the adjoining single bond.[17] If this is the case for allenes such as **4** (or **8**), and recognizing that *planar* rotamers of diradicals such as **14** are simply resonance forms of the corresponding fulvalenes, then the fulvalene should be formed, regardless of the structure of either the monomeric intermediate or the isolated dimer. In other words, diradicals such as **14** should collapse to fulvalenes faster than they do anything else. If this is the case, then there must be a mechanism for fulvalenes such as **9** to close to dimethylenecyclobutanes with the stereochemistry expected to diradicals such as **14.** One way to resolve this apparent dichotomy is a relatively facile rotation about the adjoining fulvalene double bonds which would interconvert the fulvalenes and the diradicals.[18] Of course one important consequence of this suggestion is that the structures of the dimers can say nothing about the structures of the monomers.



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Finally, it is interesting to explore why the double bonds in **13** are localized as suggested. Models clearly show that the proposed structure is much less strained than the alternative.

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Carbon-13 and Proton Hyperfine Splittings and Their Variation with Temperature for Some Alkoxyalkyl Radicals[1]

Sir:

Successive replacements of the hydrogen atoms in the planar $\dot{C}H_3$ radical by fluorine yields radicals with increasing $^{13}C_\alpha$ hyperfine splitting constants.[2] A similar phenomenon is anticipated for successive substitution of H by RO groups (R = H or alkyl). While there is a wealth of data relating to the $a(^{13}C_\alpha)$ values of monoalkoxyalkyls,[3-8] there are no such data for trialkoxymethyls and the only data relating to dialkoxyalkyls involve the radical anion of perdeuterioacetic acid in a solid matrix[9] and some five- and six-membered cyclic radicals.[6,10] Since ring strain induces deviations from planarity at C_α[5,11] and since this leads to enhanced $a(^{13}C_\alpha)$ values we have now measured $a(^{13}C_\alpha)$ for some neutral acyclic dialkoxyalkyls and for trimethoxymethyl in solution.

Our present results are compared with data from the literature in Table I. As was expected, $a(^{13}C_\alpha)$ increases with increasing substitution by RO, but the effect is less than with fluorine.[12] The similarity in $a(^{13}C_\alpha)$ values for all dialkoxyalkyls indicates that these values are not significantly influenced by ring strain in the five- and six-membered rings. The values of $a(^{13}C_\alpha)$ for the di- and trialkoxyalkyls support the view that these radicals are nonplanar.

The temperature dependence of the hyperfine coupling constants, $a(^{13}C_\alpha)$ and $a(H_\alpha)$, can yield important information regarding the configuration[13] of the radical in question,[11,14,15] since the variation in a with temperature arises primarily from out-of-plane vibrations at C_α. Thus, it is generally agreed that if $[\partial|a(^{13}C_\alpha)|/\partial T]_{T\rightarrow 0}$ is negative (cf. $(Me_3CO)_2\dot{C}H$ and $\overline{OCH_2OCH_2OC}\dot{H}$) the radical prefers a nonplanar configuration.[14-16] The sign of $\partial|a(H_\alpha)|/\partial T$, (and of the deuterium isotope effect)[17] has occasionally been used to deduce the sign of $a(H_\alpha)$.[11,19,20] We wish to draw attention to the fact that although the sign of $\partial|a(H_\alpha)|/\partial T$ is not an entirely reliable guide to the sign of $a(H_\alpha)$,[15] its sign for alicyclic $(RO)_2\dot{C}H$ radicals (−) is more consistent with $a(H_\alpha) > 0$ than with $a(H_\alpha) < 0$.[21]

For nonplanar radicals having inversional symmetry the out-of-plane vibrations are governed by a symmetric double-minimum potential function.[14,15] The temperature dependence of $a(^{13}C_\alpha)$ and of atoms directly bonded to C_α (e.g., H_α) have been discussed (with special reference to $(CH_3)_3\dot{C}$) by Wood and co-workers[14] and by Krusic and Meakin.[15] According to the general theory of the latter authors,[15] which utilizes a potential function of the form $V(q) = -aq^2 + bq^4$ ($a, b > 0$), the sign of $\partial|a(H_\alpha)|/\partial T$ will depend not only on the sign of $a(H_\alpha)$, but also on the number of vibrational states below the top of the inversion barrier *and* on the temperature of the measurements. For example, for $a(H_\alpha) > 0$, if there are at least three vibrational levels below the barrier top then $\partial|a(H_\alpha)|/\partial T$ will be negative at low and positive at high temperatures,[22] while if there are only two vibrational states below the barrier then $\partial|a(H_\alpha)|/\partial T$ will, because of zero-point effects, be positive at all temperatures.[15,23] The reverse applies if $a(H_\alpha) < 0$.

For the specific case of alicyclic $(RO)_2\dot{C}H$ radicals, the magnitude of the $a(^{13}C_\alpha)$ values indicates that the radicals are severly bent while the negative sign of $\partial|a(^{13}C_\alpha)|/\partial T$ for $(Me_3CO)_2\dot{C}H$ implies that, for this radical at least, there must be three or more vibrational levels below the barrier top[15] and, moreover, the experimental measurements must have been made in the low temperature[22] region. The fact that $\partial|a(H_\alpha)|/\partial T$ is *negative* therefore requires that $a(H_\alpha)$ is *positive* for these radicals.[25]

Finally, the magnitudes of $a(H_\alpha)$ in alicyclic $(RO)_2\dot{C}H$ (9.6–14 G), in $\overline{OCH_2CH_2OC}\dot{H}$ (21.7 G), and in $\overline{OCH_2O}$-