activated manganese dioxide. The annelated semibullvalene so obtained (**7**, calcd m/e 144.0939, found m/e 144.0941, 20% yield) was observed to undergo polymerization when exposed to the atmosphere at ambient temperature for several hours. Confirmation of structure was achieved by catalytic hydrogenation to **8**, which was identical with an authentic sample.[9] On the basis of its electronic properties [$\lambda_{\max}^{\text{isooctane}}$ 240 nm (sh) (ϵ 4600)], **7** possesses a typical semibullvalene chromophore. The nmr spectrum (Figure 1) is characterized by a 2:2:2:4:2 ratio of protons, the chemical shifts of which correspond closely to those of semibullvalene[3,6] and several of its monosubstituted derivatives.[10] We therefore conclude that the equilibrium in the case of **7** (the nmr spectrum remains invariant from −91 to +116°) is *not* weighted very heavily in that direction in which the cyclopropane ring occupies a position central to the two larger rings, but consists rather of a near equitable distribution of isomers **7a** and **7b**.

7a **7b**

[4.4.2]Propella-2,4,8,11-tetraene (**3b**),[7] readily available by suitable chemical modification[8] of the corresponding 3,8,11-triene,[11] also undergoes ready conversion to **4b**, mp 255° (75%).[7] ($_{\pi}2 + _{\pi}2$) photocyclization of the cyclobutene and bicyclo[2.2.2]octene double bonds in **4b** can be affected conveniently by triplet-sensitized (acetone) irradiation. Skeletal rearrangement of **5b**[7] to dicyclopropyl isomer **6b** was accomplished in 89% yield by heating with a 20-fold molar excess of anhydrous 0.2 *N* silver perchlorate in benzene for 60 hr in the dark. An additional double bond was introduced into the cyclohexene ring of **6b** by a bromination–dehydrobromination sequence which utilized elemental bromine in CH_2Cl_2 at −78° and 1,5-diazabicyclo-[5.4.0]undec-5-ene (DBU) in dry THF at room temperature, respectively.

Hydrolysis of **6b** and **10** was brought about through the agency of potassium hydroxide in aqueous ethylene glycol according to predescribed procedures,[6] and mild oxidation of the resulting hydrazo compounds was achieved by aeration. Again, diazo decomposition occurred rapidly *via* the retro-homo Diels–Alder pathway[6] to give **9** (37%)[7] and **2** (23%),[7] respectively. To allow for ready comparison, the nmr spectra of these polyunsaturated hydrocarbons are illustrated in Figures 2 and 3. In the case of **9**, the three groups of olefinic protons and the bridgehead hydrogens appear at chemical shifts in agreement with dominance of the triene tautomer **9** (∼65%). In contrast, the spectrum of **2** points clearly to the absence of cyclopropyl character. Not only are the eight peripheral protons decidely olefinic and substantially downfield shifted relative to **9**, but H_b is shifted 0.9 ppm upfield while H_a appears 0.6 ppm to lower field. These data, in conjunction with the electronic spectrum [$\lambda_{\max}^{\text{isooctane}}$ 239 (ϵ 21,000) and 335 nm (1800)], could be construed as evidence for the presence of a diamagnetic ring current as in **2c**,[12] the shifting of the bridgehead protons then arising from their relative positions in the shielding cone and beyond the rim of the "aromatic" ring, respectively. However, this conclusion must be tempered by the similarity of the nmr spectrum of **2** with that of bicyclo-[5.4.1]dodeca-2,5,7,9,11-pentaene,[12b] an apparently nondelocalized entity. The extent of the contribution of structures **2b** and **2c** to the ground state of the pentaene remains consequently a subject for continued study. It is to be particularly noted that should **2** possess some degree of homoaromatic character, overlap of the orbitals at C_4 and C_6 would be required to be intermediate between σ and π, an unusually important 1,3 interaction which has previously been recognized in an impressive array of *charged* homoaromatic systems[2,11] but which has evaded customary physical and chemical scrutiny in an uncharged milieu because of the lack of a suitable neutral molecule.

Acknowledgment. The financial support of the National Cancer Institute is gratefully acknowledged. The authors owe thanks also to Drs. Stanley A. Lang, Jr., and Michael J. Broadhurst for assistance with the 100-MHz nmr spectra.

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[13] National Institutes of Health Predoctoral Fellow, 1969–1971.

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Crystal and Molecular Structure of [14]Annulene

Sir:

The annulenes have served as suitable objects for the interpretation of nmr spectra[1] and the testing of various theories of π bonding in cyclic conjugated systems.[2] A detailed knowledge of the molecular structures for the annulenes is invaluable in assessing both spectral measurements and theories.[3] According to Hückel's rule, [14]annulene, first synthesized by Sondheimer and Gaoni,[6] should be aromatic and most probably a planar molecule. It has been shown[7–9] that [14]annulene in solution exists as two species, each of which undergoes fast isodynamical transformations at room temperature. Oth has demonstrated recently[9] that these two species are different configurations, I and II. A two-dimensional X-ray study[10] on [14]annulene indicated that the

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[1] F. Sondheimer, I. C. Calder, J. A. Elix, Y. Gaoni, P. J. Garratt, K. Grohmann, G. di Maio, J. Mayer, M. V. Sargent, and R. Wolovsky, *Chem. Soc., Spec. Publ.*, No. **21**, 75 (1967).

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[4] S. M. Johnson and I. C. Paul, *J. Amer. Chem. Soc.*, 90, 6555 (1968); S. M. Johnson, I. C. Paul, and G. S. D. King, *J. Chem. Soc. B*, 643 (1970).

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[7] Y. Gaoni and F. Sondheimer, *Proc. Chem. Soc.*, 299 (1964).

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[10] J. Bregman, *Nature* (*London*), 194, 679 (1962).

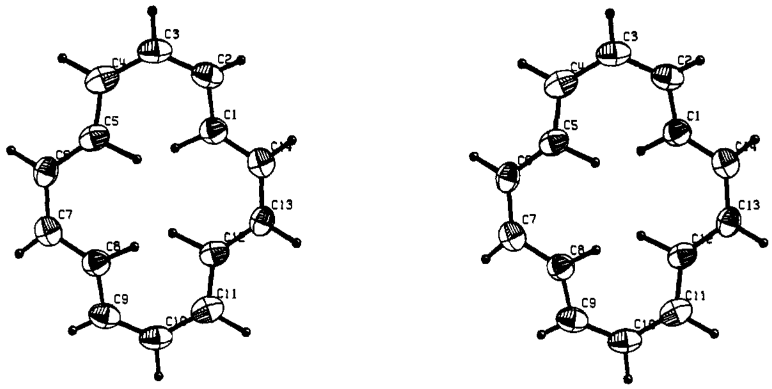


Figure 1. Stereoscopic view of a molecule of [14]annulene. The thermal ellipsoids are scaled to 25% probability.

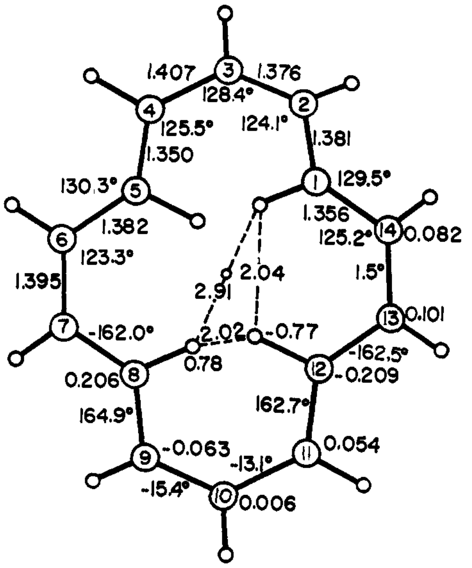
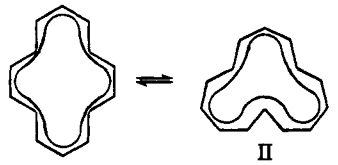


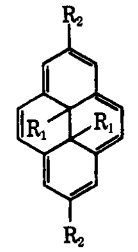
Figure 2. Molecular dimensions in [14]annulene. The upper half of the drawing shows the bond lengths (angströms) and bond angles (degrees). The lower part of the drawing (related by a center of inversion) shows the deviations of atoms (angströms) from the best plane through the carbon atoms, and the torsion angles around the C–C bonds (degrees). The esd's of the C–C bonds are 0.010 Å and of the C–C–C angles are 0.5°. According to the formula given by P. J. Huber in the appendix in E. Huber-Buser and J. D. Dunitz, *Helv. Chim. Acta*, **44**, 2027 (1961), the esd's of the torsion angles are approximately twice those of the valency angles.

molecule had configuration I in the crystal[7] and was situated on a center of symmetry but did not reveal the details of the molecular conformation. We now report the results of a three-dimensional X-ray study on [14]annulene.

The dark-red needlelike crystals of [14]annulene are monoclinic with $a = 8.640$ (2), $b = 4.376$ (2), and $c = 14.996$ (5) Å, and $\beta = 106° 5'$ (1′). There are two molecules of $C_{14}H_{14}$ in the unit cell and the space group is $P2_1/c$.[11] A total of 412 independent nonzero reflections was measured on a Picker FACS-1 diffractometer using Cu Kα radiation. The structure was solved by the symbolic addition method and has been refined by full-matrix least-squares procedures to an R factor of 0.054 on all observed data. Anisotropic temperature factors were included for the carbon atoms, while the hydrogen atoms were refined with isotropic temperature factors.



I II



IIIa, $R_1 = CH_3$
$R_2 = OCOCH_3$
b, $R_1 = CH_2CH_3$
$R_2 = H$

The molecular structure of [14]annulene in the crystal is shown in Figure 1; this structure corresponds to configuration I. Some molecular dimensions are shown in Figure 2. The molecule is clearly and significantly nonplanar with C(1) and C(5) deviating by −0.206 and 0.209 Å from the best plane through all the carbon atoms in the molecule; H(1) and H(5) deviate by −0.78 and 0.77 Å from this plane. In the crystal, the molecule is centrosymmetric but approaches C_{2h} symmetry, with the twofold axis running through atoms C(3) and C(10) (Figure 1). The cause of the significant nonplanarity is the steric overcrowding of the four internal hydrogen atoms in the center of the molecule. The H(1)---H(5), H(1)---H(12), and H(1)---H(8) distances are 2.02 (7), 2.04 (7), and 2.91 (7) Å, respectively. The C–C bond lengths range from 1.350 (11) to 1.407 (11) Å with an average value of 1.378 ± 0.019 Å. While the "spread" of the individual lengths implies possible significant differences, there is no obvious chemically significant pattern to the values obtained (*e.g.*, bond alternation as was found in [16]annulene[4]). [18]Annulene, which was much more nearly planar than [14]annulene, exhibited a range of bond lengths from 1.371 to 1.429 Å.[5] In contrast, the lengths of the perimetrical C–C bonds in two dihydropyrene derivatives III lay in a narrow range;[12] the atoms forming the peripheral skeleton in these two molecules, however, were more

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(11) In ref 10, the cell data were presented in terms of the $P2_1/a$ setting.

(12) A. W. Hanson, *Acta Crystallogr.*, **18**, 599 (1965); **23**, 476 (1967).

nearly coplanar than those in [14]annulene and had different patterns of deviations from the best plane.[13]

The distortions from planarity are distributed throughout the molecule. With the exception of the C(6)–C(7) bond, the torsion angles around the crystallographically independent half of the ring lie in the range of 10–20° (for cis bonds) and 160–170° (for trans bonds); the substituents on the C(6) and C(7) atoms are almost completely eclipsed (torsion angle = −1.5°).

The structure found herein is entirely compatible with the nmr spectrum obtained at low temperatures (a peak corresponding to four protons at τ 10.61 and a ten proton peak at τ 2.12, at −126°) for freshly dissolved [14]annulene;[8,9] an "isodynamic mobility"[9] among conformations of type I is responsible for the equivalence of all the protons at higher temperatures. Our results emphasize the need to recognize and make allowance for the high degree of nonplanarity in this $[4n + 2]$annulene when calculations of resonance energy are being made,[2] and provide a basis for such calculations.[14]

Acknowledgment. We thank Professor Franz Sondheimer and Dr. Klaus Stöckel for generously supplying us with the sample of [14]annulene.

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(13) It should be pointed out that as both [14]- and [18]annulene, IIIa and IIIb, occupy sites with crystallographic centers of symmetry, it is possible that effects arising from disorder could mask certain minor differences in bond length. No obvious evidence for disorder was found in the crystallographic studies on these molecules.

(14) The list of atomic coordinates and structure amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N. W., Washington, D. C. 20036, by referring to code number JACS-72-4741. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

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The Rate of *tert*-Butyl Rotation in 2-*tert*-Butyl 1,3-Diheteroatomic Rings. The Roles of Bond Angle and Bond Length in a Trend Reversal

Sir:

Knowledge regarding the dynamics of rotation about single bonds and conformational preference has implications in both mechanistic and synthetic chemistry. Although significant experimental[1] and theoretical[2] efforts have been expended to elucidate the origin of the potential barriers to rotation about single bonds, an incisive depiction of the barrier origin(s) is elusive even in the case of ethane.[3]

This report concerns the measurement of the rate of *tert*-butyl rotation in a series of 2-*tert*-butyl 1,3-diheteroatomic rings (1–7; Table I) indicating not only an expected dependence on the steric bulk of proximate alkyl groups and heteroatoms but also a significant dependence on the preferred geometry of the heterocycle involved.[4]

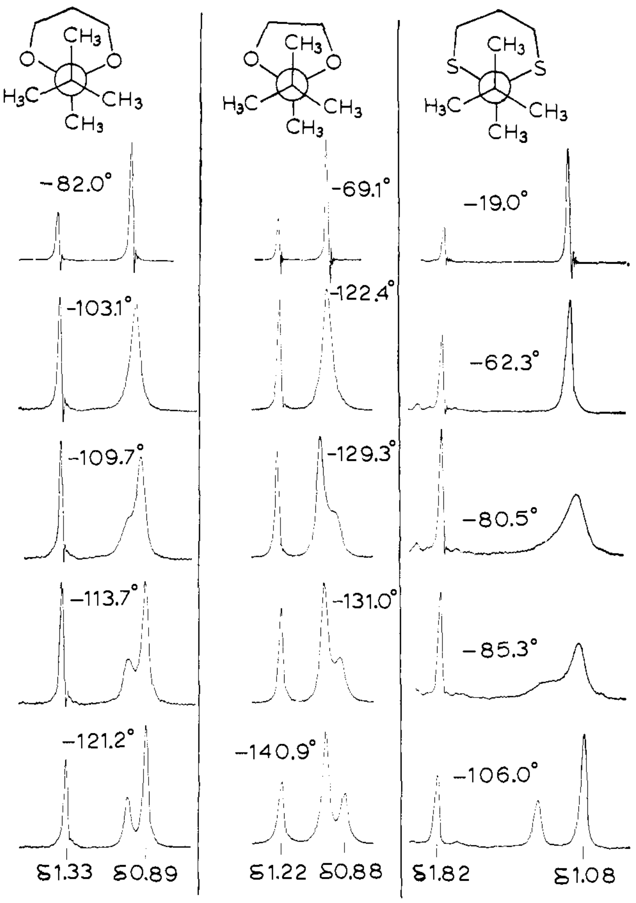
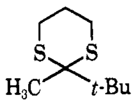


Figure 1. The ^{1}H dnmr spectrum (60 MHz) of **6**, **7**, and **1** as a function of temperature.



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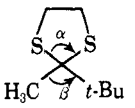

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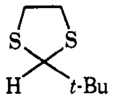

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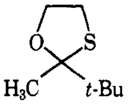

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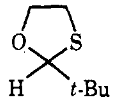

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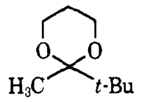

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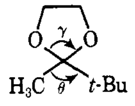

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Examination of the ^{1}H dnmr[5] spectrum (60 MHz) of **1**–**7** revealed in all cases changes in the *tert*-butyl resonance attributable to slowing of *tert*-butyl rotation. Three cases (**1**, **6**, **7**) are illustrated in Figure 1. The slow exchange chemical shifts of the methyl groups of each *tert*-butyl group (Table I) were obtained from a total line-shape analysis. Also compiled in Table I are activation parameters for *tert*-butyl rotation in **1**–**7** derived from total line-shape analyses.[6] Unfortunately, examination of the ^{1}H dnmr spectrum of 2-*tert*-butyl-1,3-dithiane, 2-*tert*-butyl-1,3-dioxane, and 2-*tert*-butyl-1,3-dioxolane revealed only broadening of the *tert*-butyl resonance with no clean peak separation at low temperatures.

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