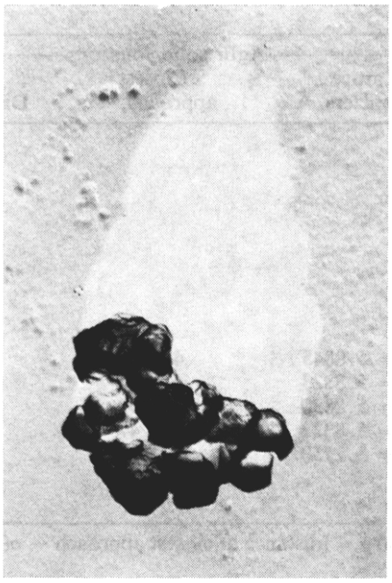

Figure 1. Electron micrograph of coprecipitated particles of 20 mol % AgI, 80 mol % AgBr. The particles were deflocculated ultrasonically. Magnification: 50,000×.

the lattice spacing in the basal plane in the hexagonal system. The disregistry expresses the difference between the atomic spacings in the close-packed plane (the 111 plane) in the cubic system and the basal plane of the ice lattice. The significance of this quantity was discussed above. In the tables, the terms AgI solid solutions and AgBr solid solutions refer to the terminal solid solutions formed with AgI and AgBr as the solvents, respectively. In Figure 2 the distances of closest approach ($a\sqrt{2}/2$) are plotted and compared to that of ice. Thus the difference between the two curves represents the packing difference in the closest packed planes, or the disregistry, between the solid solutions and the ice lattice. The component phases that are present in the X-ray powder diagrams are listed in Table II.

Table II. Compositions of AgBr–AgI Solid Solutions

Mol % AgBr	Phases present
5	AgI solid solution
10	AgI solid solution
15	AgI solid solution AgBr solid solution
30	AgI solid solution AgBr solid solution
60	AgI solid solution AgBr solid solution AgBr
85	AgBr solid solution

It is well known[5] that the leveling off of the lattice parameters in solid solutions indicates the limit of solubility of the solute in the solvent. It is clear from Figure 2 that the limit of solubility of AgBr in AgI in this experiment is approximately 28 mol % and the solubility of AgI in AgBr is approximately 30 mol %. According to the constitution diagram of Stasiw and Teltow,[4] the solubility of AgI in AgBr is about 16 mol %, while up to 50 mol % AgBr can be substituted in the AgI lattice at 127°. However, the conditions of our experiment are such that in all likelihood thermodynamic equilibrium was not reached, accounting for the high solubility of AgI in AgBr. Further studies will be reported shortly elsewhere on our observations of the ice-nucleating efficiency of these solid solutions.

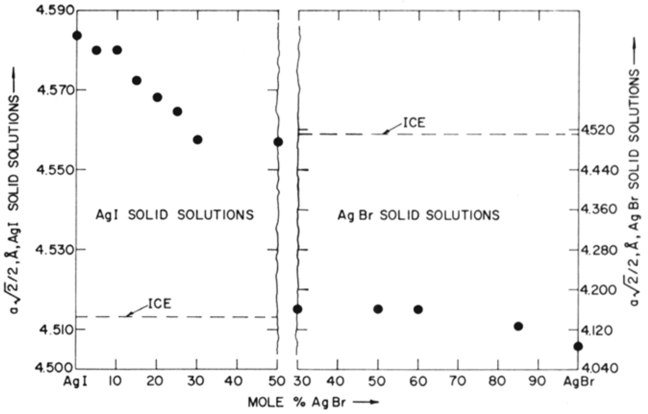

Figure 2. Average distance of closest approach in close-packed planes of AgI–AgBr solid solutions.

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[5] C. S. Barrett and T. B. Massalski, "Structure of Metals," McGraw-Hill, New York, N. Y., 1966.

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The Geometry of [10]Annulenes

Sir:

Since Hückel's prediction of aromaticity for certain monocyclic polyenes in 1931,[1] chemists' interest in [10]annulenes has been evident and attempts at the synthesis of this system date back presumably to the early part of this century when Willstätter accomplished the first synthesis of cyclooctatetraene.[2] We wish to record herein that we have now prepared two *crystalline* (below −60°) [10]annulenes, **1** and **2**, and to present evidence to establish the double bond geometry of these molecules. Temperature-dependent ^{13}C nmr spectroscopy has been employed to elucidate a unique automerization[3] of compound **2**. This instance represents one of the first—if not the first—example of its application to this type of problem.

After a critical evaluation of possible synthetic routes leading to **1** and/or **2** we reached the conclusion that one similar to that reported earlier[4] is a *practical*

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[1] E. Hückel, *Z. Phys.*, **70**, 204 (1931).

[2] R. Willstätter and E. Wase, *Ber.*, **44**, 3423 (1911).

[3] A. T. Balaban and D. Farcasiu, *J. Amer. Chem. Soc.*, **89**, 1958 (1967).

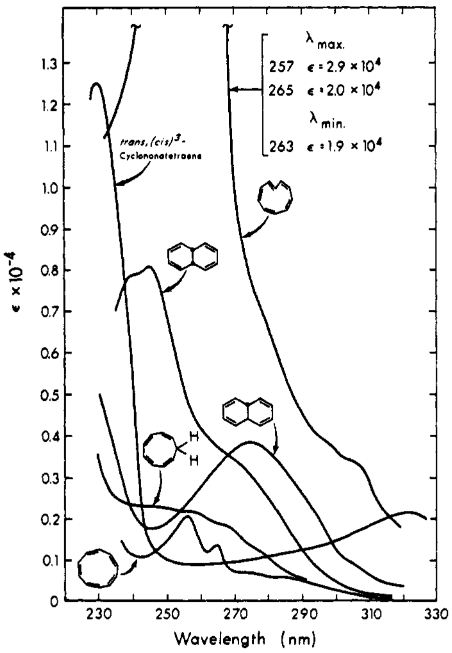

Figure 1. Uv spectra of various cyclic polyenes measured at −55° (MeOH). Concentrations of the [10]annulenes are estimated.

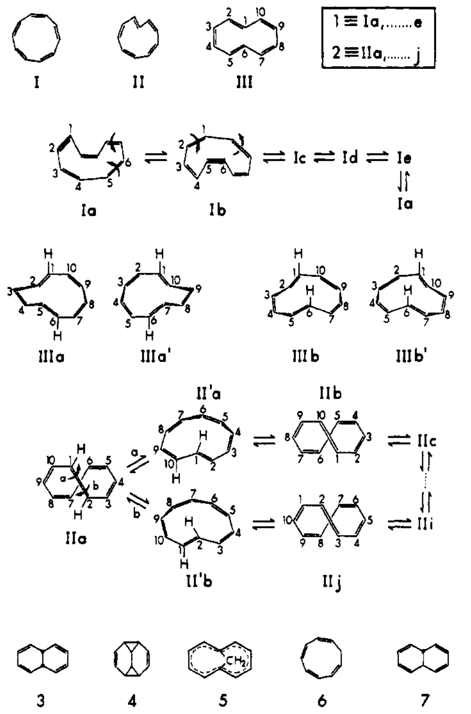

Figure 2.

method to supply a sufficient amount of the compounds for further investigation. Thus, irradiation (2537 Å) of *cis*-9,10-dihydronaphthalene (**3**) (2 *M* THF) at −60°, followed by removal of tetracyclo[4.4.0.0^{2,10}.0^{5,7}]deca-3,8-diene (**4**)[5] which crystallized at −80°, provided a [10]annulene-enriched (*ca.* 30%) mixture. Chromatography on alumina (Woelm, 1.5% wt H_2O, *n*-pentane–CH_2Cl_2 gradient) at −80° [6] separated two new crystalline compounds **1** and **2**.[7] These compounds were found not to be thermally interconvertible.

Quantitative thermal conversion of **1** into *cis*-9,10-dihydronaphthalene (**3**) was unambiguously demonstrated by the nmr and uv spectroscopy (Figure 1): $k(-14.25 \pm 0.05°$ in deuterioacetone$) = (1.28 \pm 0.06) \times 10^{-5}$ sec^{-1}; $k(6.2 \pm 0.1°) = (2.43 \pm 0.02) \times 10^{-4}$ sec^{-1}. Both ^{1}H [a singlet, τ 4.33 (THF-d_8), $W_{1/2}$ = 0.6 Hz] and ^{13}C nmr (proton-decoupled) [a singlet (δ 130.4 from TMS (THF-d_8)][8] spectra remained temperature independent over a range of −40 to −160° [THF-d_8 + $(CD_3)_2O$]. Even fine-splitting proton-coupled ^{13}C spectra[9] of **1** were virtually invariant ($J_{^{13}C-H}$ = 158 Hz).

Of eight possible combinations for the arrangement of five cis and/or trans double bonds in a ring, only three (I, II, and III, Figure 2) may be structurally possible. The equivalence of nuclei (H or C) demonstrated above strongly suggests I for **1**[10a] and further demands either the planarity of the molecule or a low-energy (presumably less than 5 kcal/mol) barrier for a process averaging magnetic environments of the nuclei.[11] The former possibility is excluded mainly on two grounds: (i) the uv spectrum of **1** is dissimilar, particularly in intensity, to that of a nearly planar system, *e.g.*, 1,6-methano[10]annulene (**5**)[12] and resembles that[13] of $(cis)^4$-cyclononatetraene (**6**) and (ii) the proton chemical shift of **1** is in the olefinic region in contrast to those exhibited by **5**.[10b,12] However, nonplanar models (*e.g.*, Ia) constructed with slight distortion of normal bond angles reveal that the automerization from Ia to Ib can be readily (through a low-energy barrier) achieved by pseudorotating the two double bonds along the single bond in the manner indicated in Figure 2. A sequence of similar processes achieves the complete averaging.[10c] This operation is reminiscent of the interconversion between twist–boat cyclohexane conformers and is quite different from that of cyclooctatetraene which proceeds through the coplanar conformation.[14] Other processes, *e.g.*, the

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(4) S. Masamune and R. T. Seidner, *Chem. Commun.*, 542 (1969); *cf.* E. E. van Tamelen and T. L. Burkoth, *J. Amer. Chem. Soc.*, **89**, 151 (1967).

(5) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *ibid.*, **90**, 5286 (1968).

(6) K. Hojo, R. T. Seidner, and S. Masamune, *ibid.*, **92**, 5641 (1970).

(7) The [10]annulene-enriched mixture (*ca.* 5 g) constituted approximately one-half of the total photolysate, and contained **1** (10%) and **2** (20%). Chromatography of the mixture readily afforded pure **2** and a fraction containing **1** and **3** only (*ca.* 1:4 ratio) essentially without the loss of the [10]annulenes that originally existed. The separation of **1** from **3** was difficult and tedious. We have thus far isolated pure **1** by repeated chromatography in amounts sufficient to permit accurate spectral measurements.

(8) T. Keller, "Compilation of C-13 Chemical Shifts," Bruker Physik, A. G. Forscheim, 1969; A. J. Jones and D. M. Grant, in preparation.

(9) J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, Elmsford, N. Y., 1968, Chapter 12.2.

(10) Omitted in this communication are: (a) obvious reasons for the exclusion of II and III for **1**; (b) some other less important grounds to reject the coplanarity of **1**; (c) a drawing of the whole cycle of this automerization; and (d) at least two additional arguments [*e.g.*, violation of the selection rule (III → 7)] disfavoring III.

(11) Accidental equivalence [δ and J (proton-coupled ^{13}C)] is highly improbable and not considered.

(12) E. Vogel and H. D. Roth, *Angew. Chem., Int. Ed. Engl.*, **3**, 228 (1964); H. D. Roth, Inang. Dissert., Köln, 1965.

(13) A. G. Anastassiou, V. Orfanos, and J. H. Gebrian, *Tetrahedron Lett.*, 4491 (1969), G. Boche, H. Böhme, and D. Martens, *Angew. Chem., Int. Ed. Engl.*, **8**, 594 (1969); E. A. LaLacette and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965); S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969); S. Masamune, K. Hojo, and S. Takada, *ibid.*, 1204 (1969).

(14) F. A. L. Anet, A. J. R. Bourn, and Y. S. Lin, *J. Amer. Chem. Soc.*, **86**, 3576 (1964).

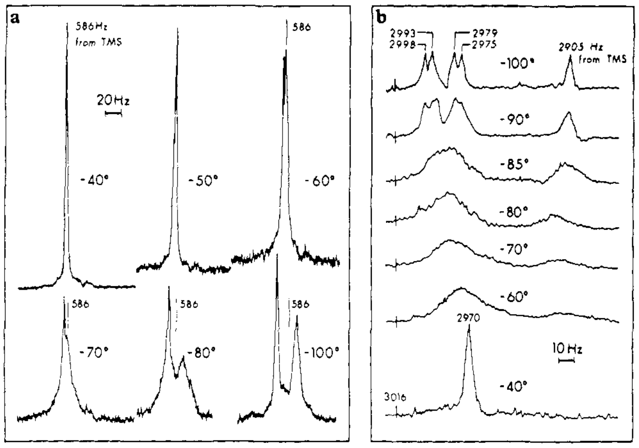

Figure 3. (a) ^1H nmr spectra of **2** (100 MHz, 3-methylpentane-d_{14}). (b) ^{13}C nmr spectra of **2** (22.63 MHz, THF-d_8).

single–double bond alternation, may be occurring concurrently, but are not demanded at present.

Compound **2** was converted quantitatively into *trans*-dihydronaphthalene (**7**): $k(-44.5 \pm 0.1°$ in acetone$) = (2.52 \pm 0.14) \times 10^{-5}$ sec^{-1}, $k(-25.5 \pm 0.1°) = (5.15 \pm 0.25) \times 10^{-4}$ sec^{-1}. Both ^1H and ^{13}C nmr spectra of **2** were temperature dependent between −40 and −100° (Figure 3) and demonstrated that **2** was frozen in a conformation below −100° and that all the nuclei of the same kind achieved equivalence at around −40° while **2** was slowly iosmerizing to **7**. Therefore, there must exist a process which permits the migration of a "trans" double bond (or bonds) around the ring to achieve a cycle of the automerization.

Of the remaining two structures, III is ruled out from the arguments that follow. (i) IIIa (C_s) and IIIb (C_2) could possibly attain higher symmetry D_{2h} and C_{2h} through a double bond shift ($1,2 \rightarrow 1,10$ and $5,6 \rightarrow 6,7$) if the rate exceeds the nmr time scale, but further migration retaining the cis,cis,trans,cis,trans geometry (*e.g.*, $1.10 \rightarrow 9,10$ and $6,7 \rightarrow 5,6$) to achieve the eventual, total equivalence is highly unlikely. Rather, IIIa and IIIb would prefer to undergo permanent isomerization yielding a bicyclo compound.[15] (ii) Models indicate the improbability of finding suitable conformers in which the van der Waals interactions both between H-1 and H-6 and between the p orbitals of C-1 and C-6 are rather insignificant without causing substantial angle strains. (iii) **2** is also obtained from cyclononatetraenide[6,18] and the presence of three consecutive cis double bonds in **2** appears secure.[10d] In contrast, Dreiding models of II indicate that there exists a stable and puckered conformer IIa (C_2), which can be converted into a less stable and near-coplanar conformer (II′a or II′b) through rotation a or b (Figure 2). The latter two (II′a and II′b) very likely provide pathways leading from IIa to IIb and IIj, thus the original 1,2-*trans*,-(*cis*)^4-[10]annulene is now converted into 1,10-*trans*,-(*cis*)^4- or 2,3-*trans*,(*cis*)^4-[10]annulene. Obviously then, through conformers similar to II′a or II′b (which are presumably close to a transition state of this automerization) one trans double bond can rotate along the ring, all the nuclei (H or C) of the system ultimately achieving equivalence.[10c] Comparison of the ^{13}C spectra with those computer simulated on the basis of the above mechanism[19] lends strong support to our interpretation that only one process (transfer of one double bond to the next position) is responsible for their temperature variance.[20,22]

We have isolated **1** and **2** and have established their structures and stereochemistry. One can now conclude without reservation that the [10]annulenes by no means belong to the category of aromatic compounds. The kinetic data for the thermolyses of **1** and **2** now confirm our previous statement that thermolyses of all the compounds (*e.g.*, **1**, **2**, and **4**) involved in the photolysis of **3** and **7** are essentially quenched below −50°.[4] Photochemically induced interconversions between **1** and **2** proposed earlier[4] are now verified experimentally and do proceed very rapidly. The rates are comparable to those of photocyclization of **1** and **2** to give bicyclo compounds such as **3** and **7**. The rates of these cyclizations relative to those of the (photochemical) ring opening of the bicyclo compounds are, at minimum, one order of magnitude greater over a wide range of concentrations at −100° and these *relative* rates decrease as the temperature increases. Therefore, while at −110° or below we observed the formation of [10]annulenes only in trace amounts (at any stage of the photolysis of the bicyclo compounds), **1** and **2** accumulated substantially at −50 to −60°. Thus our earlier observation noted during the study of the photochemistry of $(CH)_{10}$ hydrocarbons is understood to some extent.

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[15] We are implicitly postulating that the low-energy single–double bond alternation of cyclic polyenes normally proceeds through a coplanar or near-coplanar transition state.[16] An exception is the case where the π overlapping of localized double bonds is severely diminished in the ground state due to the strain involved.[17]

[16] J. F. M. Oth and J. M. Gilles, *Tetrahedron Lett.*, 6259 (1968).

[17] E. H. White, E. W. Friend, R. L. Stern, and H. Maskill, *J. Amer. Chem. Soc.*, **91**, 523 (1969).

[18] T. J. Katz, J. J. Cheung, and N. Acton, *ibid.*, **92**, 6643 (1970).

[19] Spectra were simulated as a function of lifetime using the Block phenomenological equations modified to account for exchange (S. Meiboom, *J. Chem. Phys.*, **34**, 375 (1961); H. M. McConnell, *ibid.*, **28**, 430 (1958)). Details will be described in a full paper.

[20] The mechanism of the conversion of bicyclo[6.2.0]deca-2,4,6,9-tetraene into **7**[21] will be discussed in light of this finding in a future publication.

[21] S. Masamune, C. G. Chin, K. Hojo, and R. T. Seidner, *J. Amer. Chem. Soc.*, **89**, 4804 (1967).

[22] A referee advised us that some comment on the differences in the uv spectra exhibited by **1** and **2** should be inserted in this note. We are not able to develop any sophisticated quantum mechanical argument on this point. We can only offer an obvious interpretation at present. The coplanarity of a part of **2** (two or three double bonds) is attained to a greater extent than in **1**. It is interesting to note that a similar trend was observed for a pair of compounds, **6** and *trans*,(*cis*)^3-cyclononatetraene (Figure 1).[13]