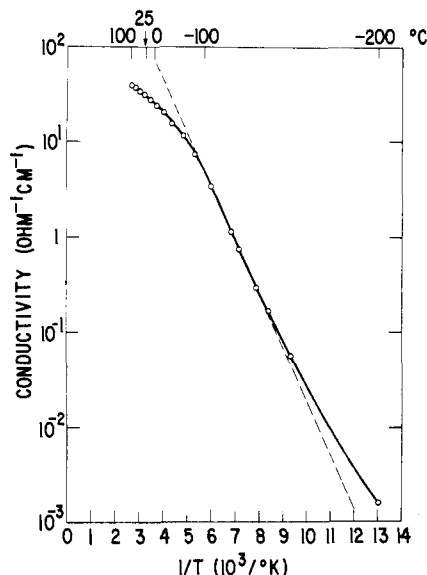


**Figure 1.** Projection of the  $\text{TTT}_{1.2}\text{NiS}_4\text{C}_4\text{H}_4$  structure on the  $ab$  plane. Ni indicates positions of the Ni and two of the S atoms of the  $\text{NiS}_4\text{C}_4\text{H}_4$  unit. These S atoms lie, respectively, above and below the Ni in the actual structure.



**Figure 2.** Conductivity ( $\sigma$ ) of a  $\text{TTT}_{1.2}\text{NiS}_4\text{C}_4\text{H}_4$  crystal as a function of temperature. The dashed line, which indicates the region of maximum slope of  $\log \sigma$  vs.  $1/T$ , is drawn to illustrate the nonlinear character of the  $\log \sigma$  vs.  $1/T$  dependence.

ecules of TTT to 1.0  $\text{NiS}_4\text{C}_4\text{H}_4$ . The complete structure has not yet been refined, but the structural parameters are known sufficiently well to specify the molecular arrangement. It is shown in Figure 1 in terms of the smaller subcell appropriate for  $\text{NiS}_4\text{C}_4\text{H}_4$  for which  $a = 12.73 \text{ \AA}$ ,  $b = 22.13 \text{ \AA}$ , and  $c = 8.73 \text{ \AA}$ , space group  $C222_1$ , with  $Z = 4 \text{ NiS}_4\text{C}_4\text{H}_4$  and 4.8 TTT. The plane of the TTT molecules is almost parallel to the  $ab$  plane with a uniform separation of  $3.63 \text{ \AA}$ . The  $\text{NiS}_4\text{C}_4\text{H}_4$  molecules are in planes perpendicular to  $b$  with two sulfur atoms in the  $ab$  plane and two above and below Ni. There are two distinct orientations for the  $C_2$  axis which bisects the dithiolene chelate rings at ca.  $45^\circ$  to the  $c$  axis. There is no stacking of  $\text{NiS}_4\text{C}_4\text{H}_4$  molecules nor are there any close contacts between them.

The apparently uniform stacking arrangement of TTT units along  $c$  is analogous to that found in  $\text{TTT}_{1.5}$ <sup>7</sup> as well as that observed for other highly conductive organic D-A compounds.<sup>2</sup> The absence of structurally distinguishable  $\text{TTT}^+$  and TTT units is suggestive of a delocalized electronic arrangement in the TTT substructure.

The temperature dependence of the dc conductivity (Figure 2) is also analogous to that previously found for other 1-D conductors below the peak in conductivity vs.  $T$ , which is associated with the cross-over from 1-D metal to Peierls semiconductor behavior in many of these compounds.<sup>2,8</sup> In the case of  $\text{TTT}_{1.2}\text{NiS}_4\text{C}_4\text{H}_4$ , the conductivity reaches  $30 \text{ ohm}^{-1} \text{ cm}^{-1}$  at  $25^\circ \text{ C}$  and continues to increase, with increasing tempera-

ture, up to the point of thermal decomposition of the sample ( $\sim 180^\circ \text{ C}$ ), suggesting a cross-over to 1-D metallic conductivity behavior in a temperature range which is substantially higher than that typically found for 1-D metal systems.<sup>2,8</sup>

The results of the physical property measurements, in the context of the apparently uniform TTT stacking arrangement found in the structure, are strongly suggestive of a 1-D metal system with a highly correlated 1-D distortion<sup>2,8</sup> such that a gap in the electronic excitation spectrum exists up to the thermal decomposition point of the sample. The existence of such an energy gap could lead to the observed quenching of the  $\text{TTT}^+$  unpaired spins as well as to the thermally activated conductivity behavior observed up to  $180^\circ \text{ C}$ .

The detailed nature of the 1-D distortions which produce this energy gap and the possible role of the  $\text{NiS}_4\text{C}_4\text{H}_4^-$  spin subsystem in determining the unusually high temperature range for the metal-insulator transition are among the important questions which await more detailed studies on this compound.

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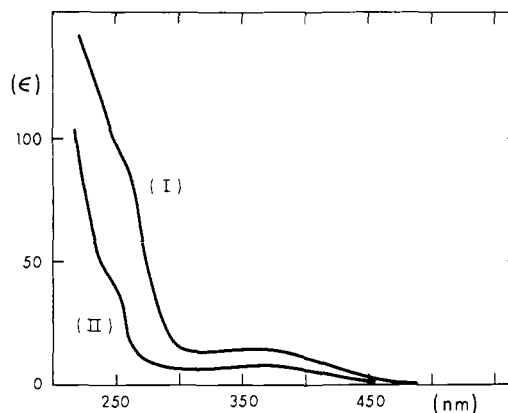
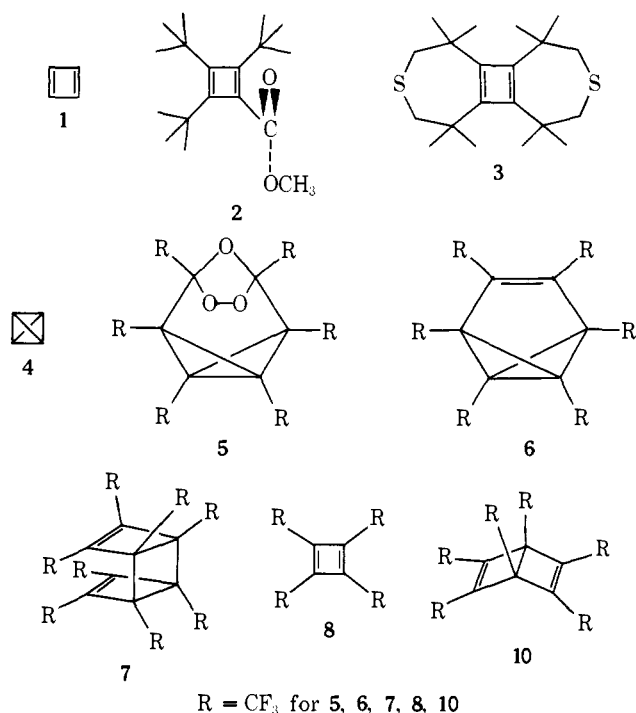
## The [4]Annulene (Cyclobutadiene) System. The Tetrakis(trifluoromethyl) Derivative

Sir:

The chemistry of [4]annulene (**1**) continues to present an experimental challenge and to attract theoretical interest.<sup>1</sup> The full characterization of two simple derivatives (**2** and **3**) has recently been completed and provides unequivocal evidence

that these compounds possess singlet ground states, and that their geometries are not square, but approximately rectangular.<sup>2,3</sup> These results contrast with those of the parent compound. While the ground state of **1** is almost certainly singlet,<sup>2a</sup> an analysis of its infrared spectrum has led to the conclusion that **1** detained in an argon matrix at ca. 10 K has a square geometry.<sup>4</sup> It should be pointed out, however, that the arguments are now found to rest mainly on the appearance of just one apparent C–C stretching vibration at 1240 cm<sup>-1</sup>.<sup>5</sup> Theoretical treatments of this system have appeared from time to time in the past,<sup>1a</sup> and more recently a few interesting proposals have been advanced to accommodate what appears to be mutually inconsistent results—singlet ground state but square geometry.<sup>6a,b</sup> A definitive, purely theoretical solution of **1** requires further improvement in the treatment of the system, however. An additional important problem associated with **1** is the relationship with its valence isomer, tetrahedrane(tricyclo[1,1,0,0<sup>2,4</sup>]butane) (**4**). Maier in his review article<sup>1b</sup> states (without evidence) that irradiation of some photolabile bicyclobutane derivatives first produces intermediates which then thermally rearrange to give the corresponding [4]annulene derivatives. With two objectives in mind, (i) to follow the fate of the biradical or its synthetic equivalent corresponding to **4** and (ii) to characterize fourfold symmetrically substituted derivatives of **1** and possibly **4**, we have investigated the photolysis of the ozonide (**5**) of hexakis(trifluoromethyl)benzvalene (**6**)<sup>7,8</sup> at low temperatures (4–90 K). This note describes our findings.

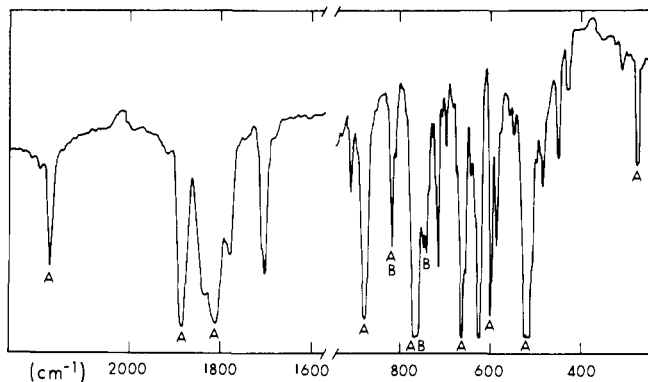
Kobayashi et al. have already shown that irradiation of **5** in a 3-methylpentane matrix at 77 K followed by thawing provided the syn-dimer **7** of tetrakis(trifluoromethyl)[4]annulene (**8**) and have postulated the intermediacy of **8** in this reaction.<sup>8a</sup> In order to be able to fully characterize **8** spectroscopically, the choice of solvent is very important in that **5** and its related perfluoro compounds have limited solubilities at low temperatures in most of the common solvents that meet the usual criteria for spectral measurements. Of numerous systems examined, hexafluoropropene (mp 117 K and bp 243 K) has been selected for UV and NMR spectra, and 3-methylpentane or a 1:1:1:1 mixture of methylcyclohexane, pentane, 2-methylbutane, and 3-methylpentane for the recording of IR absorptions in specified regions.<sup>9</sup> Thus, irradiation of **5** in a nearly



**Figure 1.** (I) A UV spectrum of **8** (photolysate I) in hexafluoropropene measured at 130 K. (II) **8** in an argon matrix (photolysate II) measured at ca. 10 K and corrected for **9**. The concentration of **8** is estimated from the UV spectrum of **5** taken before irradiation and also based on the 100% photoconversion.

transparent matrix<sup>10</sup> was performed at 77 K with a medium-pressure Hg lamp, using a filter of either Pyrex or a combination of NiSO<sub>4</sub>, K<sub>2</sub>CrO<sub>4</sub>, potassium biphthalate, and Corex.<sup>11</sup> (The photolysate obtained at this temperature is designated as I.) The photolysis was completed within 2 h and warming the matrix to 135 K provided a yellow solution of I. There were observed in the <sup>19</sup>F spectrum only two signals (both sharp singlets) at  $\delta(\text{CFCl}_3)$  69.0 and 78.7 ppm, the latter being attributable to the CF<sub>3</sub> group of trifluoroacetic anhydride (**9**).<sup>12</sup> Upon further warming, the two signals at 63.6 and 65.7 ppm, both characteristic of **7**,<sup>8a</sup> appeared at the expense of the signal at 69.0 ppm, while the one at 78.7 ppm remained unchanged. This thermal conversion proceeded slowly (with a half-life of several hours) at 145 K and very rapidly at 203 K. Obviously <sup>13</sup>C spectral data<sup>10</sup> would provide more structural information concerning the above thermally labile compound, although the signals due to the CF<sub>3</sub> groups are likely to be masked by those of the solvent employed. In addition to a singlet at  $\delta(\text{Me}_4\text{Si})$  151.5 ppm due to **9**, I exhibited at 143 K another singlet at 135.7 ppm, which upon warming lost its intensity at a rate approximately the same as that described above for the fluorine signal. These spectral data,<sup>13,14</sup> coupled with the observation that **7** formed in quantitative spectral yield (75% isolated in our hands),<sup>8a</sup> permit the assignment of structure **8**, tetrakis(trifluoromethyl)[4]annulene, to the elusive species.

The exclusive formation of **8** and **9** from **5** has encouraged us to record a solution UV spectrum of photolysate I at 130 ± 5 K as is shown in Figure 1. The 100% conversion of **5** into **8** is assumed to calculate the intensity. Somewhat surprisingly the intensity of the spectrum of **8** is low even at 230 nm, but expectedly a weak absorption extends over the visible region. The possibility that **8** and **9** form a donor–acceptor complex<sup>15</sup> is rather remote for several reasons: (1) **8** is obviously an ineffective donor compared with **1** and its tetramethyl derivative, (2) the interaction of a donor–acceptor pair observed for the [4]annulene system is normally weak and has been observed only in a matrix where the two species are generated in close proximity, (3) the C=O vibration (*vide infra*) of **9** is unperturbed in the presence of **8**, and finally (4) the UV spectra both in solution and matrix (90 K) are essentially identical. The low intensity of the spectrum clearly suggests that the absorption in the visible region corresponds to formally forbidden transitions, and therefore it is not inconsistent with the theoretical prediction made for a singlet [4]annulene in view of the approximation used in the calculation.<sup>16</sup> The UV absorption of **8** of course disappeared upon warming. The IR spectrum (135 K) shown in Figure 2 has been carefully examined against the solvent background. The region below 900 cm<sup>-1</sup> serves as a



**Figure 2.** An IR spectrum of **8** in 3-methylpentane taken at 135 K. The absorptions due to **9** and the solvent are indicated by A and B, respectively.

finger print and above  $1500\text{ cm}^{-1}$  the presence of a medium absorption at  $1700\text{ cm}^{-1}$  deserves attention (*vide infra*).

Photochemical reactions of **5** at 4–10 K duplicate approximately those performed at 77 K, but the formation of an additional minor product is noticeable. Thus, the 4 K photolysate (designated as **II**), after being warmed to 135 K, exhibited an additional  $^{19}\text{F}$  NMR signal at  $\delta(\text{CFCl}_3)$  60.2 ppm and its intensity was approximately one-tenth of that assigned to **8** (*vide supra*). This new signal disappeared at around 220 K, but the fate of this thermolysis is not yet clear. The IR spectrum of **II** in an argon matrix contained some minor absorptions in addition to those of **8**, and the overall intensity of its UV absorption was definitely less intense than what one expects with the 100% conversion of **5** into **8**, even when all possible errors in measurement are taken into account. While the formation of this new, minor product is definite and its identification is highly desirable, one can safely state at this stage that the main (90% or more) photoproduct at 4 K is **8**, and not the corresponding tetrahedrane derivative.

Tetrakis(trifluoromethyl)[4]annulene (**8**) is the first symmetrically substituted derivative of **1**, whose full spectral characterization has been completed. It has a singlet ground state. If the assignment of the IR band at  $1700\text{ cm}^{-1}$  (*vide supra*) to the  $\text{C}=\text{C}$  stretching vibration proves to be correct,<sup>17</sup> then the geometry of **8** is not square, but rectangular. The present study has also demonstrated that the direct irradiation of **8** at low temperatures does not lead to the formation of the tetrahedrane system at least as a major course of reaction,<sup>1b</sup> but rather to that of a species which undergoes the 1,3 bond cleavage of the bicyclobutane system.<sup>18</sup>

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- (10) Approximately 10 or 20  $\mu\text{L}$  of **5** in 0.5 mL of the solvent for  $^{19}\text{F}$  NMR (solvent lock) and 90  $\mu\text{L}$  in 1.5 mL for  $^{13}\text{C}$  NMR ( $^{19}\text{F}$ -decoupling at 69.0 ppm, acetone- $d_6$  in  $\text{CHFCl}_2$  lock) were used.
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- (12)  $^{19}\text{F}$  NMR spectra of **5** are temperature dependent.
- (13) For  $^{19}\text{F}$  NMR spectral data of reference compounds ( $\delta$  in bracket): **6**,  $\delta(\text{CFCl}_3)$  55.8, 58.6, and 62.5 (1:1:1) in tetrahydrofuran- $d_6$ ; **7**,  $\delta(\text{CFCl}_3)$  64.7 and 66.8 (1:1) in  $\text{C}_6\text{F}_6$  ( $\delta$  166.5); hexakis(trifluoromethyl)bicyclo[2.2.0]hexane (**10**),  $\delta(\text{CFCl}_3)$  66.0 and 66.5 (2:1) in pentane, 65.4 and 66.0 in tetrahydrofuran- $d_6$ . See also ref 8a; (a) J. A. Ross, R. P. Seiders, and D. M. Lemal, *J. Am. Chem. Soc.*, **98**, 4325 (1976); (b) Y. Kobayashi, I. Kumadaki, A. Ohsawa, and Y. Sekine, *Tetrahedron Lett.*, 2841 (1974).
- (14) For  $^{13}\text{C}$  NMR spectral data of reference compounds: **6**,  $\delta(\text{Me}_4\text{Si})$  139.2 ( $\text{sp}^2\text{ C}$ ), 121.2 ( $\text{CF}_3$  groups), 66.8, and 53.5 (tetrahydrofuran- $d_6$ ); **10**,  $\delta(\text{Me}_4\text{Si})$  123.0, 119.3, 143.1 ( $\text{sp}^2\text{ C}$ ), and 60.3 (tetrahydrofuran- $d_6$ ).
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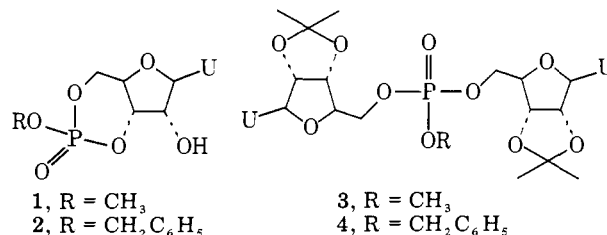
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## Synthesis of Oligoribonucleotides Based on the Facile Cleavage of Methyl Phosphotriester Intermediates

Sir:

One significant aspect of oligoribonucleotide synthesis is the development of new protecting groups<sup>1,2</sup> for the phosphate, hydroxyl, and amino moieties, for example the masking of phosphodiester intermediates as specifically designed triesters ( $\beta,\beta,\beta$ -trichloroethyl ester,  $\beta$ -cyanoethyl ester, phenoxy esters) from which the parent is obtained by the action of either a reducing<sup>1,3</sup> or a distinctly alkaline reagent.<sup>1,4</sup> We wish to report that the methyl group may serve as an alternate protecting group for phosphodiester, offering the advantage of selective removal under very mild conditions, without phosphate isomerization.<sup>5</sup> This method represents the first directed chemical synthesis of oligoribonucleotides of defined sequence using an  $\text{S}_{\text{N}}2$ -based cleavage of a phosphate protecting group.

The ability of thiolate to cleave carboxylate esters<sup>6</sup> and in particular simple phosphate triesters<sup>7</sup> suggested that the method could be used synthetically in the production of oligoribonucleotides. Indeed, it was found that lithium thiophenoxide demethylates or debenzylates triesters **1–4** very effi-



ciently (>95%) in THF/HMPA at ambient temperature within 30 min. It was later observed that the dealkylation proceeds under even milder conditions, where thiophenoxide