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Perspectives

R. B. Woodward's unfinished symphony: designing organic superconductors (1975–79)☆

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Introduction

When Robert Burns Woodward passed away in July 1979, he left behind 699 pages of hand-written notes in a neat stack in his top desk drawer. These notes were kept safely by his youngest son Eric Woodward in a small cardboard box for many years while the family pondered what to do with them. In 2001, Woodward's two grand daughters digitally scanned each page and numbered them in the order in which they were left in the original stack to protect the images for archival purposes. The notes were written on all different sorts of paper, including hotel stationary, yellowed paper pads, white photocopy paper and light blue paper. These notes revealed that RBW was deeply immersed in an astonishing project that had consumed him during the last years of his life. He became passionately interested in designing, de novo, molecules that would be organic superconducting materials.

From interviews with the Woodward family, and some colleagues, it was apparent that RBW had difficulty convincing co-workers at Harvard, as well as at the Woodward Research Institute in Basel, Switzerland, to engage in much experimental work on the ideas he was formulating. Nonetheless, RBW appeared to press on thinking deeply about unique new structures that might have the capacity to efficiently conduct electricity.

After extensive discussions with the Woodward family, permission was secured to identify a close colleague or former co-worker of RBW, with expertise in this area, to examine these notes carefully and write a retrospective view of this last, unfinished

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☆ The actual scans of R. B. Woodward's notes are property of Eric and Crystal Woodward and shall not be published nor reproduced for commercial purposes without their permission.

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work of RBW. Prof. Michael P. Cava, a former graduate student of Woodward's at Harvard, stepped forward to tackle this assignment. The accompanying paper, which primarily covers structures with, which Prof. Cava was most comfortable commenting on, is but a small sampling of the myriad ideas Woodward put on paper. I hope that the complete set of these notes will one day reach the chemical community; it is of significant historical significance.

Woodward was best known of course, for his published work on natural products structure determination and their total synthesis. What is stunning about these notes is the mathematical and geometrical depth with, which Woodward was conceptualizing conducting materials. Roald Hoffmann interacted with Woodward from time-to-time on this project over the years and Hoffmann's Preface to this article adds significant depth, color, and perspective. Only two papers were published by Woodward in this area; the vast bulk of his ideas in this field, were deprived of ever having been experimentally tested. One can not help wondering had Woodward lived longer, what advances he might have pioneered in this field. This article, and the accompanying scanned images from his notes, give an amazing glimpse of Woodward's thought process, creativity, and deep intellectual gifts that characterized his brilliant career.

Robert M. Williams
Colorado State University

Preface

Robert Burns Woodward—an architect of desire at his drawing desk

In the last three years of his life, R. B. Woodward was gripped by the idea of designing and synthesizing an organic superconductor. The evidence to that creative obsession (and I use the word in its most positive sense) is to be found in the hundreds of meticulous drawings of molecules he left behind at his untimely death in 1979. These drawings, and the associated geometrical and algebraic ruminations, effectively comprise a sketch book, tracing the creative path of a great scientist impelled by molecular desire. In an architectonic way, Woodward's blue and yellow pages represent the working through of the design of electronic function. By a master builder of molecules. Ergo the architect, and his drawing desk.

Organic conductors were hot in the mid-1970s. As yet they were a negative contribution to the gross domestic product of the countries where they were studied. No one had yet made an organic superconductor of any transition temperature of note. Buckminsterfullerene, not to speak of its salts, was just a theoretician's dream.

Yet Woodward was moved by that dream, and seized on the curious $(SN)_x$ system, as inorganic as it was organic, and on two-dimensional all-carbon lattices as starting points in his intellectual game. In the molecules he designed you see the workings of the organic imagination at its best, creative flights of molecular fancy. For example, if $(SN)_x$ did not have a handle on it, then the isoelectronic $(SCR)_x$ would. And what an incredible variety of structures surface once this ingenious molecular architect set his mind to it!

The properties desired were conductivity and superconductivity. And now Woodward was faced with a problem—not chemists, but theoretical physicists shaped the language and the ways of thinking about conductivity. Band structures, electron mobilities, scattering off phonons, Fermi surfaces were not part of the language of chemists.

Woodward found a model a chemist could wrap his mind around, Little's graphic concept of a chain of radicals surrounded by polarizable material, and the availability of vibrations decreasing electron repulsion. RBW complemented this picture by the drawing of resonance structures—in these pages we see him tirelessly redrawing the molecules to display the resonance structures rippling across them.

We don't see many molecular orbitals; this is interesting. For the facility RBW acquired in orbital thinking, beginning with the ferrocene story and the octant rule, was reinforced by the interaction he and I had in the orbital symmetry control story. In that marvelous collaboration, I was transformed from a calculator of MOs to a builder of chemical explanations based on them and their interactions.

But there were so many MOs in 1-D, 2-D, and 3-D extended structures, the real and hypothetical polymers adorning Woodward' pages. A single molecular orbital at the Fermi level did not have the 'power' to influence anything. One had to find a way of thinking about bunches of orbitals, a language that bridged solid state physics thinking with frontier orbital arguments. And at first RBW did not command that language. He drew me into the problem by asking questions. For the first time in seven years (the long Angewandte Chemie account of our work was published in 1969) we worked together. A brilliant postdoc of mine from Korea via Canada, Myung-Hwan Whangbo, was drawn to the project. He wrote our first extended Hückel theory band program. And he, I, and RBW began to try to understand bands in a chemical way.

For me, it was the beginning of a path I am still on—from bands to bonds and back again, shaping understanding at the interface of chemistry and physics.

One thing you see at intervals in the Woodward organic conductor pages is a working out of algebraic sums—favorable electron counts, interlayer spacings, the geometric constraints in the fitting in a molecule into a polygon. At various times in his life, RBW said that he flirted with mathematics when he was young. That if he had not become a chemist, he would have been a mathematician. His old love, his fearlessness—no, delight—in mathematical complication, is evident in these pages.

And the drawings! I found one page in the set that is carelessly done. It's mine. Woodward's are precise, drawn with extreme care. In free-hand lines, firmly straight where they should be, in polygons, even shaded and colored in, as in his fillings of the plane with 24-membered $C_6S_6N_{12}$ rings, the architectonic imagination soars in these drawings.

In another context, it may not be surprising that the children of this molecular architect and his artist wife would become an artist and an architect.

Like many people, Woodward had trouble translating his dreams into reality. The stellar young people who gravitated from around the world toward his Cambridge lab, often with their own support, came (and had been sent there) to gain mastery in organic synthesis. Main-group and polymer chemistry that were needed to make the SCN polymers were not part of the skill set of these young acolytes.

In Basel, Ciba–Geigy had set up a laboratory for Woodward's research. The co-workers here were more senior researchers, and in principle should do whatever RBW wanted them to do. But even if Ciba–Geigy was committed to a free-ranging Woodward, organic conducting systems were too much for them. The Woodward Research Institute group made a pair of fascinating molecules mentioned in this paper, and published the work after RBW's death. But somehow the features of interest evident in the structures of these molecules did not make an impression on the team or their sponsors. The work was not followed up.

No point in thinking about the attractive paths that the chemistry of conducting materials could have taken, would have taken had Woodward lived. Let's be thankful for what is given to us in these crumbling yellow and blue pages. In them I see evidence of an inventive mind roaming widely, searching for an organic way to think about conductivity, designing in this microuniverse of chemistry singular molecules that are simply beautiful. And … still waiting to be made.

The greatest molecular architect of the 20th century is in these pages groping for understanding. What fun it is to follow his imagination!

Roald Hoffmann
Cornell University

Woodward's Thoughts, Drawings, and Work on Potential Organic Superconductors

The early seventies essentially saw the birth of the area of organic conductors. The first one of these to draw wide attention was the crystalline tetrathiafulvalene–tetracyanoquinodimethane (TTF–TCNQ) complex **1** (Fig. 1), in which the radical cations from TTF and the radical anions from TCNQ stack like pancakes and conductivity occurs in one dimension with no significant interstack electronic interaction.[1] Graphite has also been known to be an electrical conductor, a semimetal, for a considerably long time.

Next was the inorganic polymer $(SN)_x$ (**2**), derived from the sulfur analog of nitric oxide(NO), which was an intrinsic metallic conductor[2] became slightly better conducting after oxidation with bromine (Fig. 2).[5]

Polyacetylene (**3**) has been known for a long time. However, its conducting behavior upon oxidation was discovered in 1968[3] but only in 1977 were films doped to high conductivity;[4] it may be viewed as $(CH)_x$, essentially the prototype of polymeric conducting materials.[4]

The properties of these materials attracted the attention of none other than R. B. Woodward (often referred to as RBW in this paper), one of the greatest chemists of the last century. In this article, we have made a modest attempt to present some of his ideas in this area, based upon his preliminary unpublished notes made available to us, through the courtesy of his family.

Woodward's exploration of conducting organic materials was cut short by his untimely death in 1979. We will return later to an important experimental paper based on his research, but in Woodward's lifetime, only a single paper was published growing out of his extensive considerations. In that paper, Whangbo, Hoffmann, and Woodward[5] looked at a variety of known organic conductors—graphite, polyacetylene, polydiacetylenes, polyacenes, polyphenylenes, $(SN)_x$—and explored the electronic structure of just a very few of the infinite networks designed by Woodward that we will encounter in this paper.

Woodward began by thinking about graphite, polyacetylene, and $(SN)_x$. We can see some of his grappling with the electronic structure in three pages from his notes, Figs. 3–5 In Fig. 3 he makes a reference to the Little model. This is a theoretical model of superconductivity by W. A. Little,[6] that is, particularly easy for chemists to understand. It begins with a chain of radicals, and then purports to explain how the electron–electron repulsion that a neighboring electron of the chain of radicals experiences as it hops from radical site to radical site is decreased or removed. The repulsion can be reduced, or even turned into an attraction—thus inducing superconductivity—by the polarizability of the chemical groups attached to the chain supporting the radicals. Thus a translation for chemists of the physicists' idea of strong-excitonic-coupling helping a material becomes superconducting.

The most attractive aspect of the hundreds of pages of unpublished work by RBW involves the proposal of countless structural modifications of the known conducting polymers of that period, and the design of entirely new networks, some likely to be conducting. In the following sections we shall delineate these ideas. Many of these have not materialized. In recent times, however, several close modifications have been conceived independently by other workers who have published their results. We shall make an attempt to include references to such related work as well.

1. Modifications of $(SN)_x$

Polythiazyl $(SN)_x$, is a well-known inorganic material derived from N=S, the sulfur analog of nitric oxide.[2] In 1973, it was discovered that upon treatment with an oxidizing agent, such as bromine, $(SN)_x$, became conducting.[7] The structure of $(SN)_x$ was assumed to be **2** (Fig. 2).

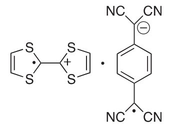


Fig. 1. Structure 1.

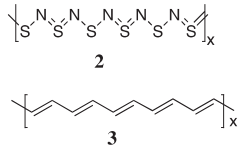


Fig. 2. Structures 2 and 3.

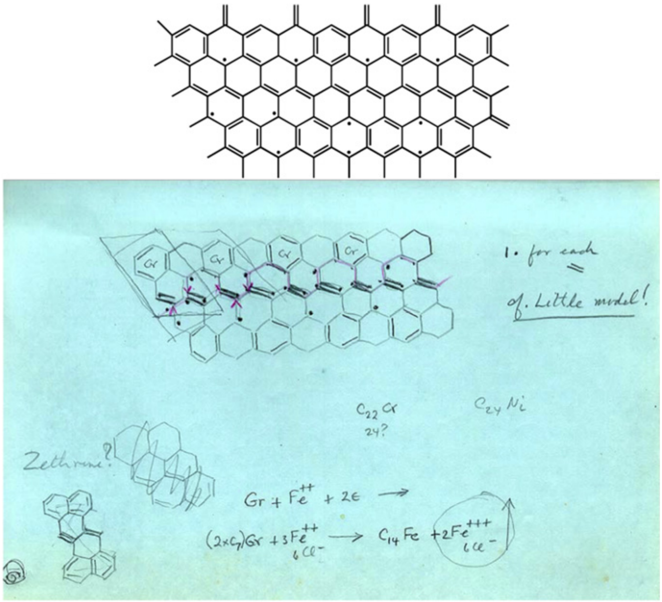


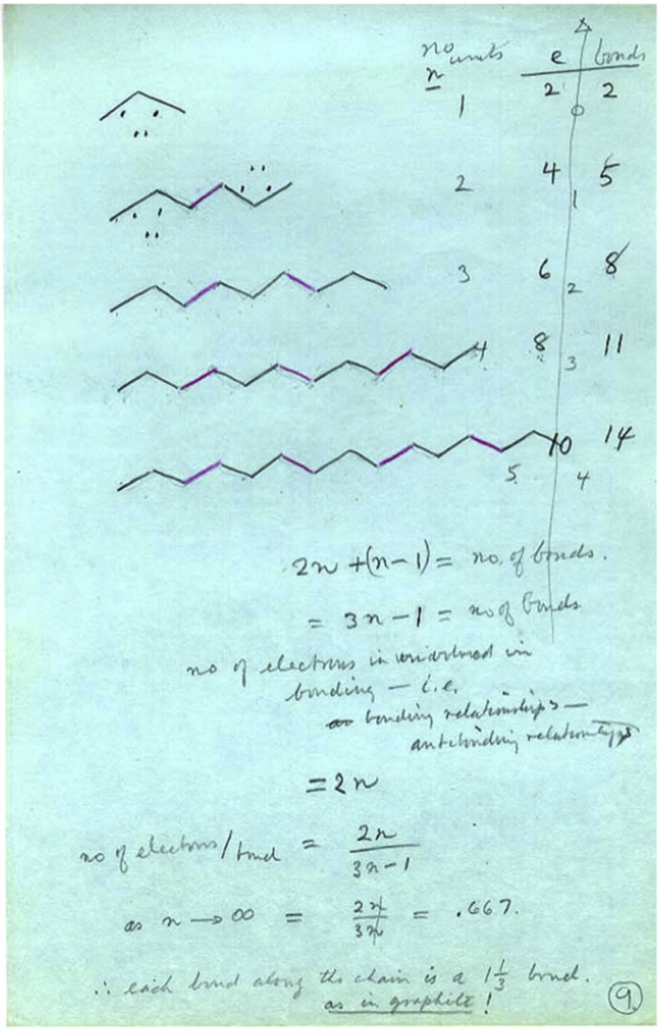
Fig. 3. Graphite structure and RBW notes, p 16.

One proposed modification was to introduce a vinyl carbon function, CR, in place of one sulfur to give a polymer of structure **4** (Fig. 6).

Such a polymer could conceivably be formed from an intermediate **5**, derived from the reaction of an amidine and sulfur dichloride (Fig. 7).

Incorporation of the –N=S=N– moiety into rings, chains etc. was also considered. Some examples of such entities are shown in structures **6**–**17** (Figs. 8 and 9) and many more appear in numerous pages of the notes; some of these are collected in Table 1 and give a snapshot of some of RBW's imagination and curiosity with regard to how these N/S materials might be constructed (Fig. 9).

Although numerous modifications of $(SN)_x$ were envisioned during Woodward's lifetime, practically none of these have as yet materialized in the literature. In a paper published in 1981 by



no units n | e | bonds

1 2 2

2 4 5

3 6 8

4 8 11

5 10 14

2n + (n − 1) = no. of bonds.

= 3n − 1 = no of bonds

no of electrons involved in bonding — i.e. bonding relationships — antibonding relationships

= 2n

no of electrons / bond = $\frac{2n}{3n-1}$

as n → ∞ = $\frac{2n}{3n}$ = .667.

∴ each bond along the chain is a $1\frac{1}{3}$ bond. as in graphite!

⑨

Fig. 4. Polyacetylene and RBW notes, p 9.

Woodward and co-workers from Harvard, Ciba–Geigy and the Woodward Research Institute in Basel, the reaction of amidine with sulfur dichloride was shown to be very complex and no polymer was produced. However, the reaction of benzamidine (**18**) with sulfur dichloride gave a very low yield of an unusual eight-membered heterocycle **19**, the structure of, which was confirmed by X-ray analysis[8] (Fig. 10).

The eight-membered ring was practically flat, and all the S–N distances were equal as were the C–N bond lengths, indicative of a delocalized 10π-electron aromatic system. In contrast, the reaction of *N*,*N*-dimethylguanidine and sulfur dichloride furnished **20** (Fig. 11), analogous to **19**, although its crystal structure showed a puckering due to folding along a central S–S axis.

The UV–vis spectra of **19** and **20** were distinct. The photoelectron spectrum (PES) of **19** and **20** were determined subsequently by several groups. Ab initio calculations were also carried out and found to be in agreement with the experimental results from X-ray photoelectron spectroscopy. The basic parent ring system is aromatic and has a planar structure.[9] However, structure **20** as well as the *tert*-butyl-substituted derivative, preferred a puckered geometry with a transannular S–S bond. The factors that influence the geometric preferences of this fascinating ring system, related to S_4N_4, remain to be elucidated.

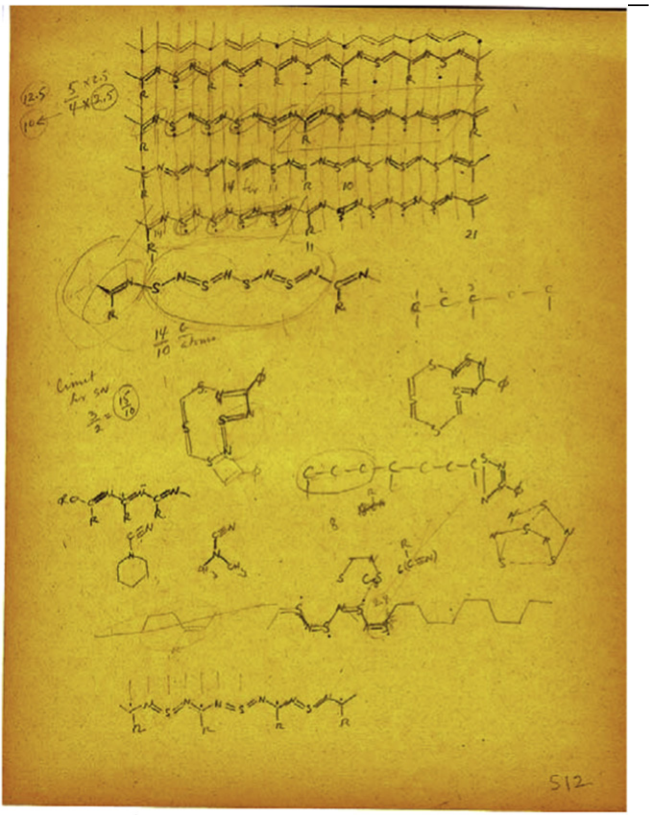
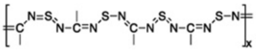


Fig. 5. RBW notes, p 512.



$[\,C{-}N{=}S{-}N{-}C{=}N{-}S{-}N{-}C{-}N{-}S{-}N{-}C{=}N{-}S{-}N\,]_x$

4

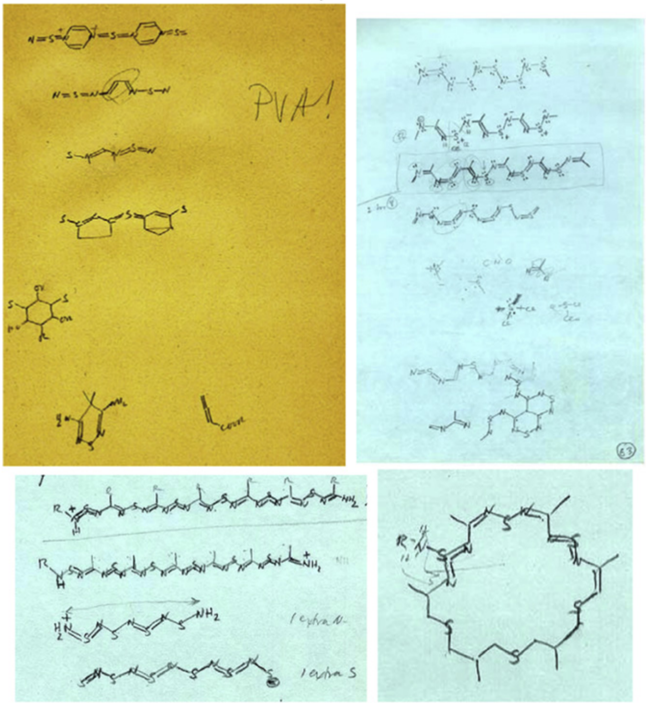
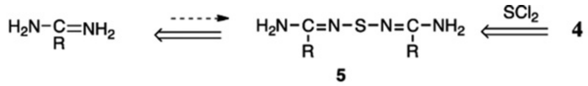
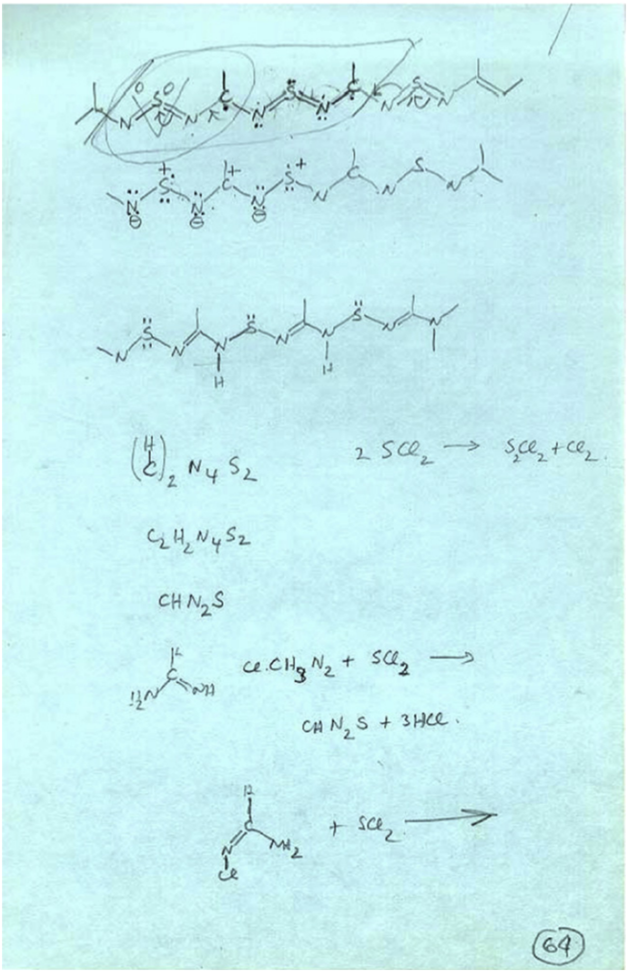


Fig. 6. Polythiazyl and RBW notes, p 1, 63, 83.



$H_2N-\underset{R}{C}=NH_2 \Longleftarrow H_2N-\underset{R}{C}=N-S-N=\underset{R}{C}-NH_2 \overset{SCl_2}{\Longleftarrow} 4$



$(\overset{H}{C})_2 N_4 S_2$

$2 SCl_2 \rightarrow S_2Cl_2 + Cl_2$

$C_2H_2N_4S_2$

CHN_2S

$Cl.CH_3N_2 + SCl_2 \rightarrow$

$CHN_2S + 3HCl.$

$+ SCl_2 \rightarrow$

(64)

Fig. 7. RBW notes, p 64.

Improved synthetic methods have also been reported as well as the isolation of a new product **21** (Fig. 12) from the reaction of benzamidine or its N–S trimethylsilyl derivative with sulfur chloride. Indeed, **21** was the major product in this reaction.[10]

Some selenium analogs have also been reported.[11] Heterocycle **8** has been studied since 1980 from both the synthetic and theoretical points of view.[12] The N_4S molecule **9** has also been subjected to theoretical calculations.[13]

Benzobisthiadiazole **11** was first reported in 1994 and was subsequently the subject of theoretical studies.[14] Several selenium analogs are also known. Some derivatives of **11** bearing electron-donating groups are highly colored, because of their low HOMO–LUMO gap.

Bisthiadiazine **12** was described in 1978.[15] Subsequently a number of theoretical studies and experimental verifications via X-ray, PES, CV, ESY etc. were carried out.[15,16] Thiadiazolo thiadazole **13** has been known from 1975 and is a very stable molecule.[17] It has attracted its share of attention from theoretical chemists.[14c,18]

There exist two references to the sulfur–nitrogen heterocycle **22**. The first pertains to the calculation in 1988 of topological resonance energies of S–N heterocycles.[19] The second is the synthesis of an analog, **23**, isoelectronic with **22** (Fig. 13).[20]

The oligomeric/polymeric phenylene thiodimide is not known diphenylsulfur dimides however, have been described, and well characterized since 1961.[21]

Woodward's thoughts appear to have focused on the 24-membered heterocycle **24** (Fig. 14; yet unknown) and isoelectronic analogs. In the hypothetical molecule **24**, three sulfurs can be considered internal (S_i), as opposed to the three external ones (S), which fall on the vertices of an isosceles triangle. The S_i–S_i distance can be calculated easily using simple trigonometrical principles, and using standard –N=C–N– bond lengths and bond angles; It is approximately 7.64 Å. The center point of this triangle is also the center point of the 24-membered heterocycle.

It was Woodward's concept (Fig. 15) that in order to force the formation of the 24-membered ring, guanidine could be used as a template, which utilizes the propensity of hydrogen-bonding between the ring N and the guanidine N–H bond.

Triaminoborane was also considered. However, it is an unknown molecule and all indications are that it is an unstable entity.

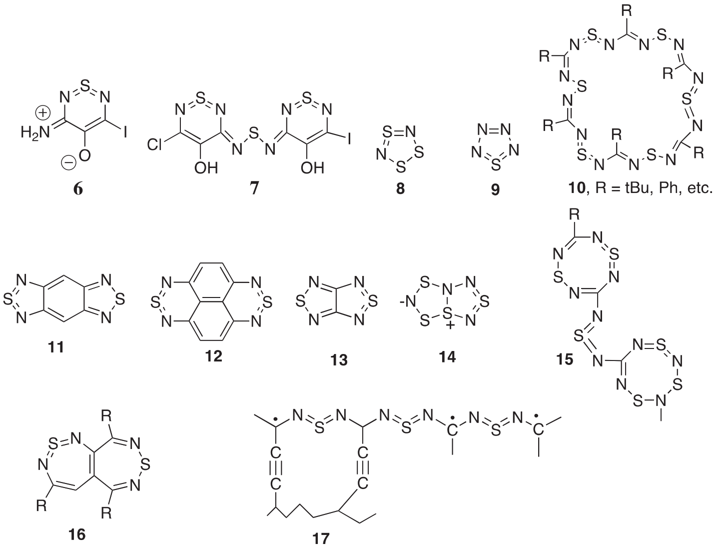


Fig. 8. Some ring structures for $(SN)_x$.

Table 1
Some N–S structures from the RBW notes

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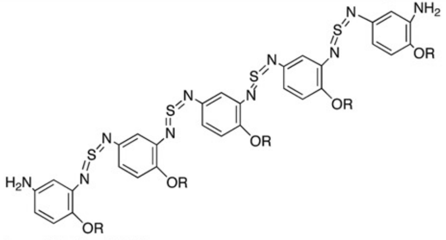
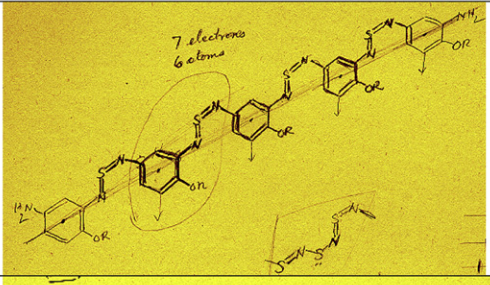
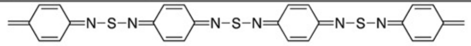
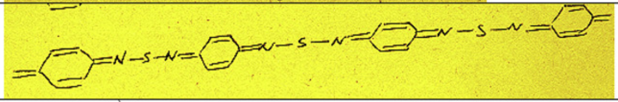
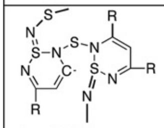
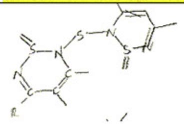
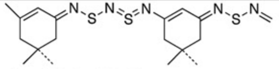
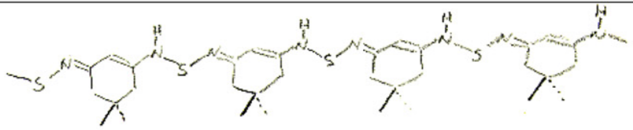
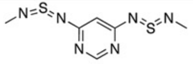
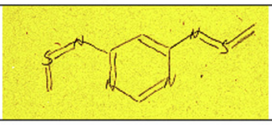
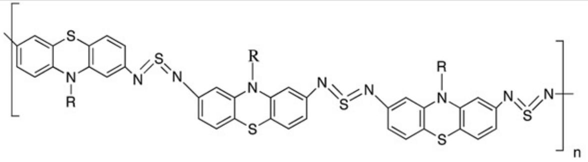
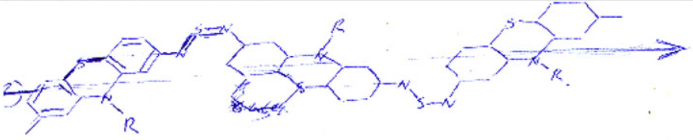
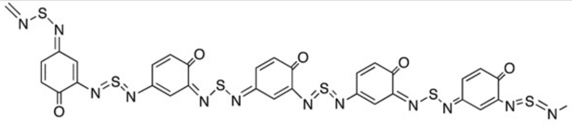
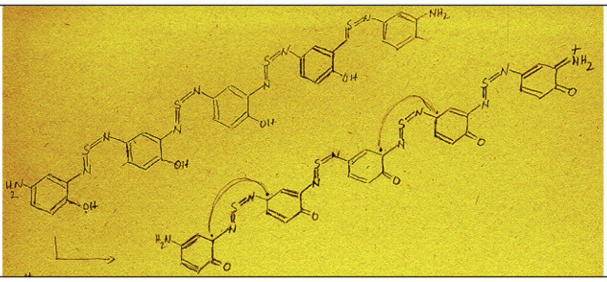
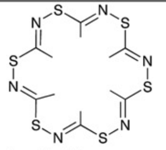
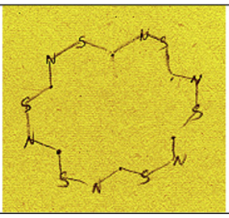
 (p. 184, 185)	
 (p. 187)	
 (p. 209)	
 (p. 210; 213)	
 (p. 260)	
 (p. 214)	
 (p. 185)	
 (p. 348)	

Table 1 (*continued*)

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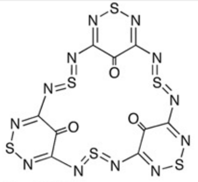
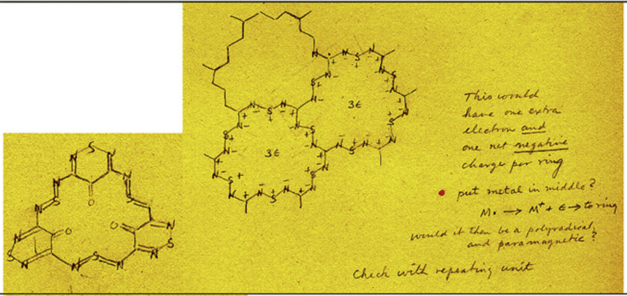
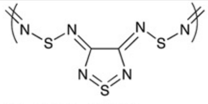
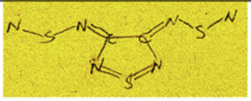
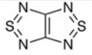
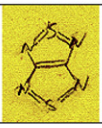
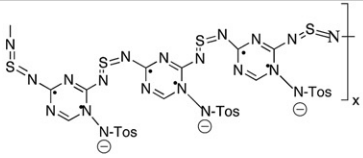
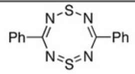
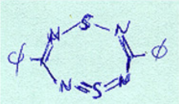
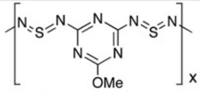
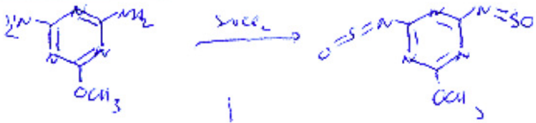
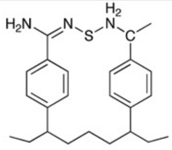
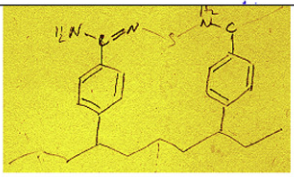
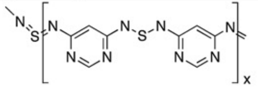
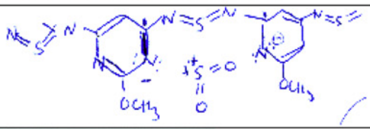
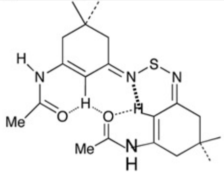
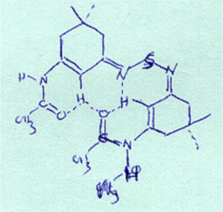
 (p. 351)	 This would have one extra electron ~~and~~ one net negative charge per ring • put metal in middle? $M\cdot \rightarrow M^{+} + e \rightarrow$ to ring would it then be a polyradical and paramagnetic? Check with repeating unit
 (p. 125; 355)	
 (p. 355)	
 (p.211; 601)	 HOTEL DREI KÖNIGE AM RHEIN BASEL
 (p. 151)	
 (p. 152; 217)	
 (p. 235)	
 (p. 217)	
 (p. 166)	

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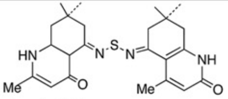
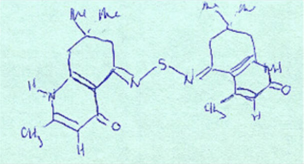
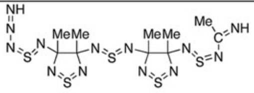
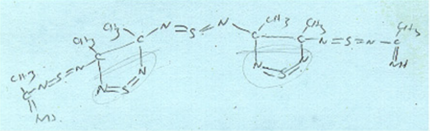
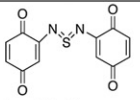
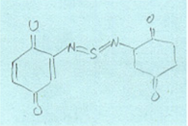
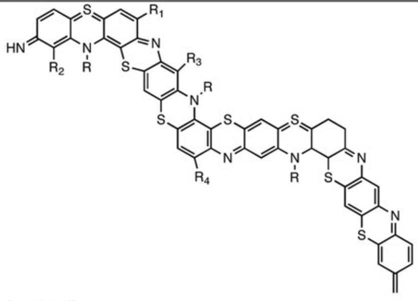
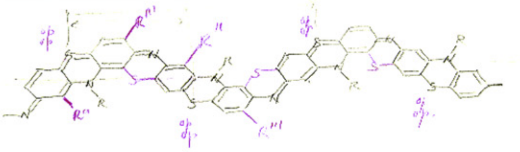
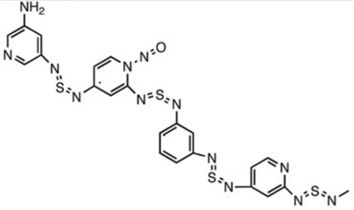
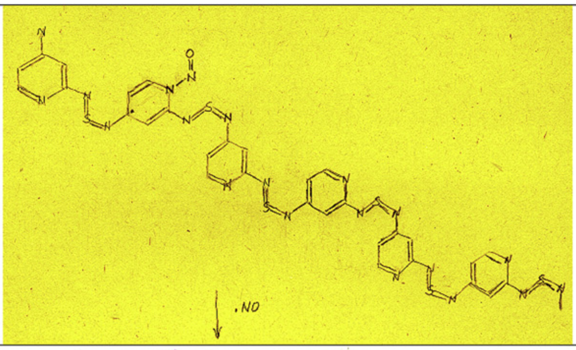
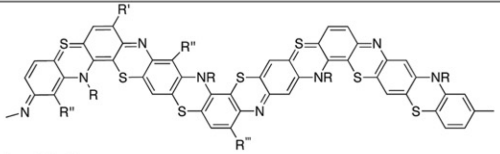
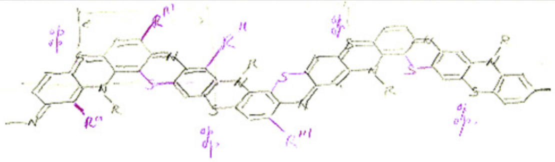
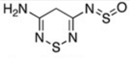
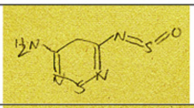
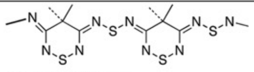
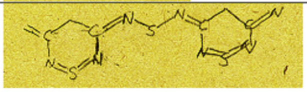
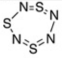
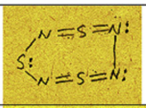
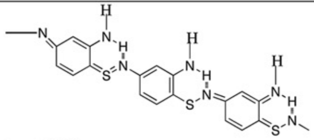
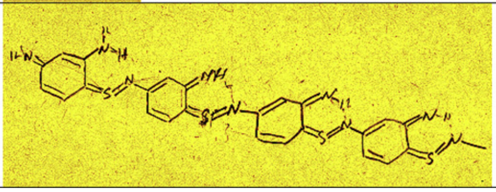
Table 1 (*continued*)

Structure & Notes Page #	Original Image RBW Notes
 (p. 167)	
 (p. 125)	
 (p. 146)	
 (p. 216)	
 (p. 262)	
 (p. 216)	
 (p. 357)	
 (p. 358; 361)	
 (p. 513)	
 (p. 600)	

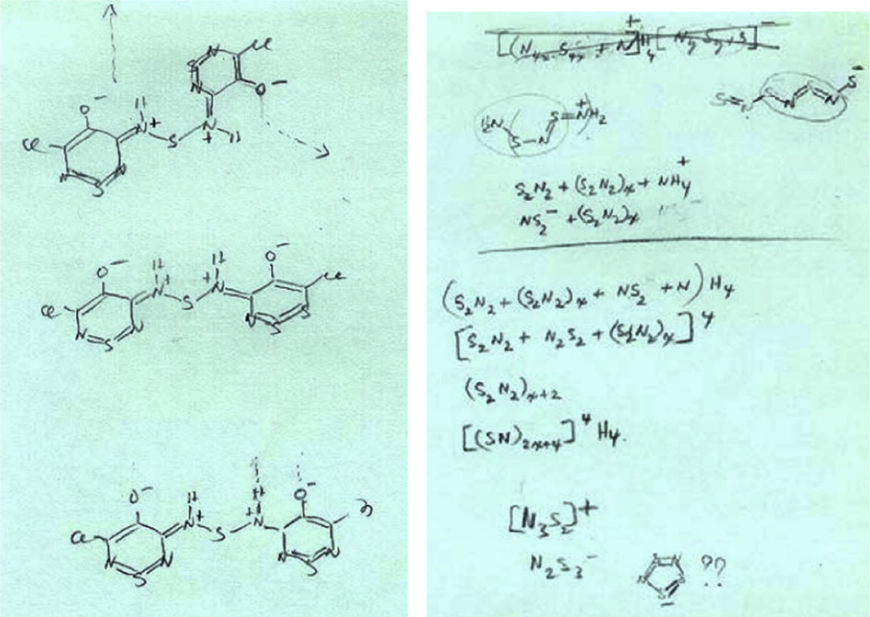
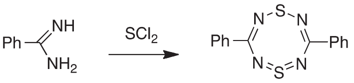
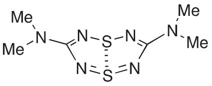


Fig. 9. Some selected structures from Fig. 8 from the RBW notes.



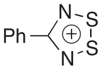
18 **19**

Fig. 10. Heterocycle reported by Woodward and co-workers in Ref. 8.



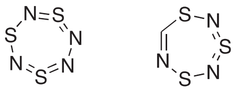
20

Fig. 11. Structure 20.



21

Fig. 12. Heterocycle reported in Ref. 8.

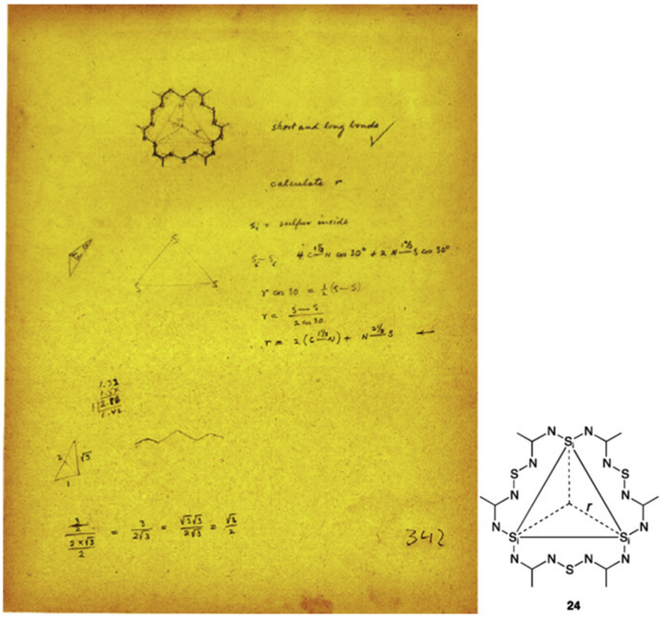


22 **23**

Fig. 13. Isoelectronic seven-membered ring heterocycles.

Networks of the 24-membered heterocycle were also considered (and beautifully rendered; see Fig. 16). The electronic structure of the infinite network of Fig. 16, $C_6S_6N_{12}$, is the last structure studied theoretically in the Whangbo, Woodward, and Hoffmann paper already mentioned.[5]

The networks envisioned by Woodward share bonds. It is tempting for the authors to speculate on a different network bonding at the C of –N=C–N– moiety to give **25** (Fig. 17).



24

Fig. 14. 24-Membered heterocycle **24**; RBW notes, p 342.

The potential stacking scenario of the 24-membered heterocycle was also considered by Woodward (see Fig. 18). By virtue of the increased electronegativity of nitrogen in comparison to carbon and sulfur, the positive charges can be expected to reside preferentially on sulfur and carbon atoms and the negative charges on the nitrogen. Therefore, these 24-membered rings can be expected to exhibit good stacking properties, as shown in **26** and Fig. 18.

In the above hypothetical $R_6C_6N_{12}S_6$ molecule, it should be pointed out that the six sulfur atoms fall on the vertices of a regular hexagon. Again using the principles of geometry and trigonometry with the known values of the C=N and C–N bond lengths and the –N–C=N– bond angle (120°), the distance between S_1 and S_2

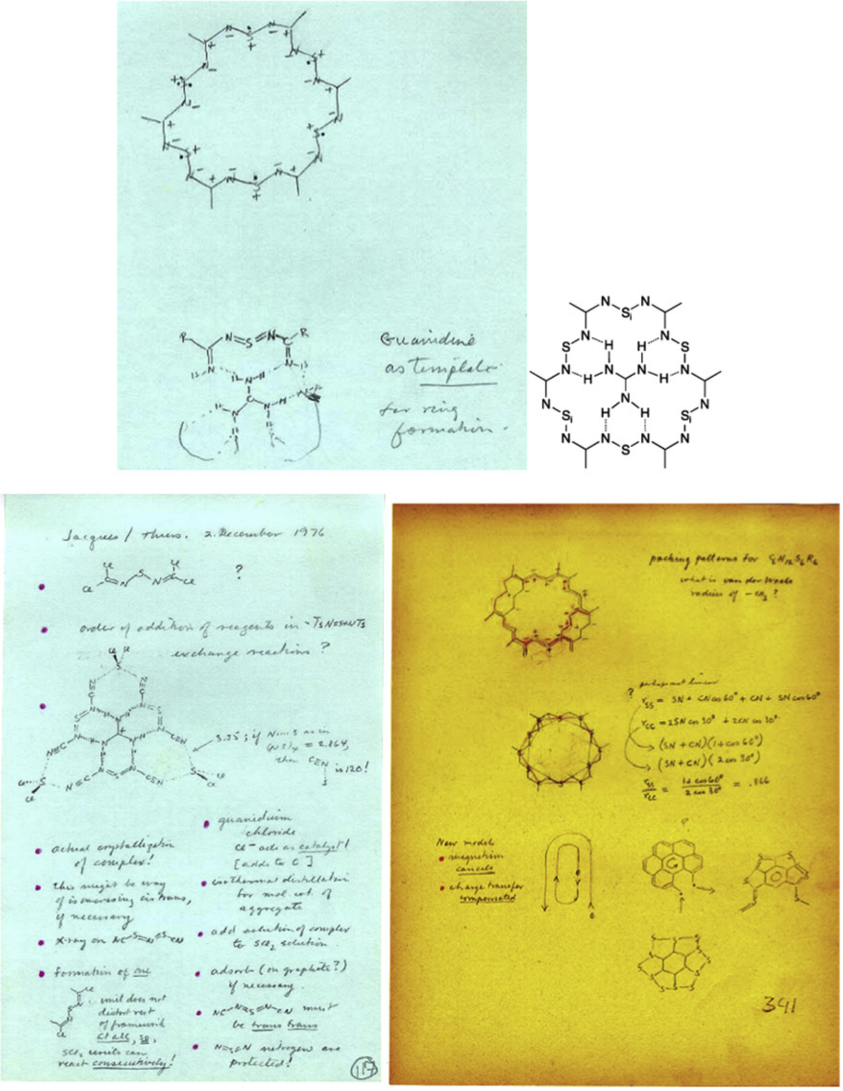


Fig. 15. RBW notes, p 82, 117, 341.

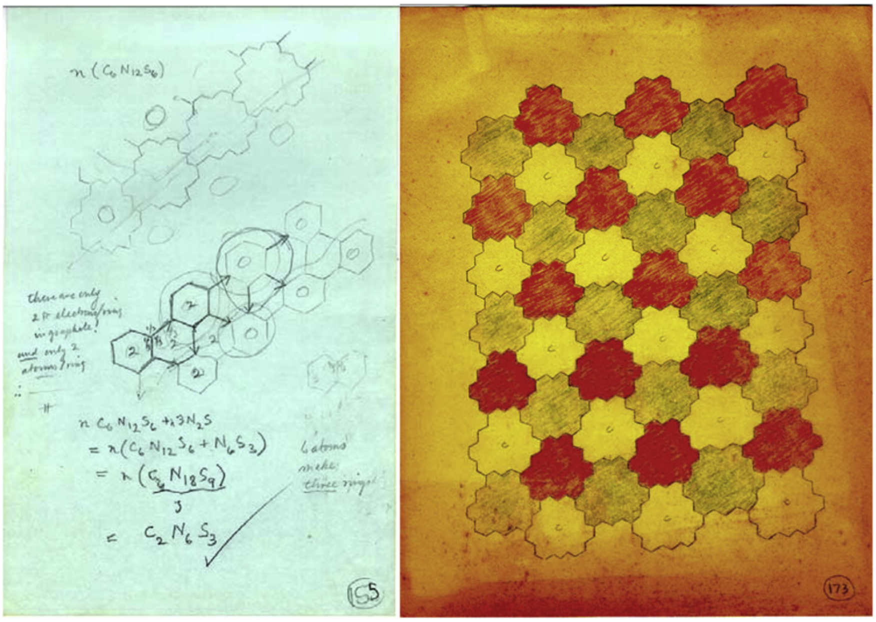
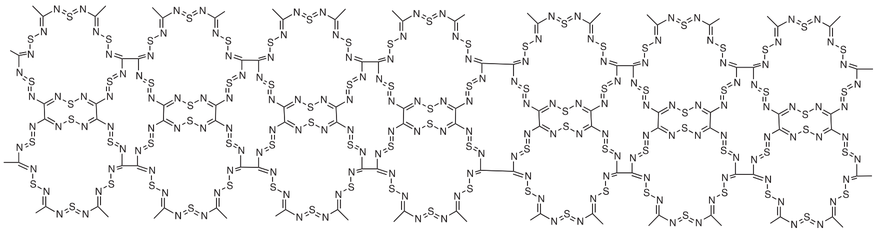
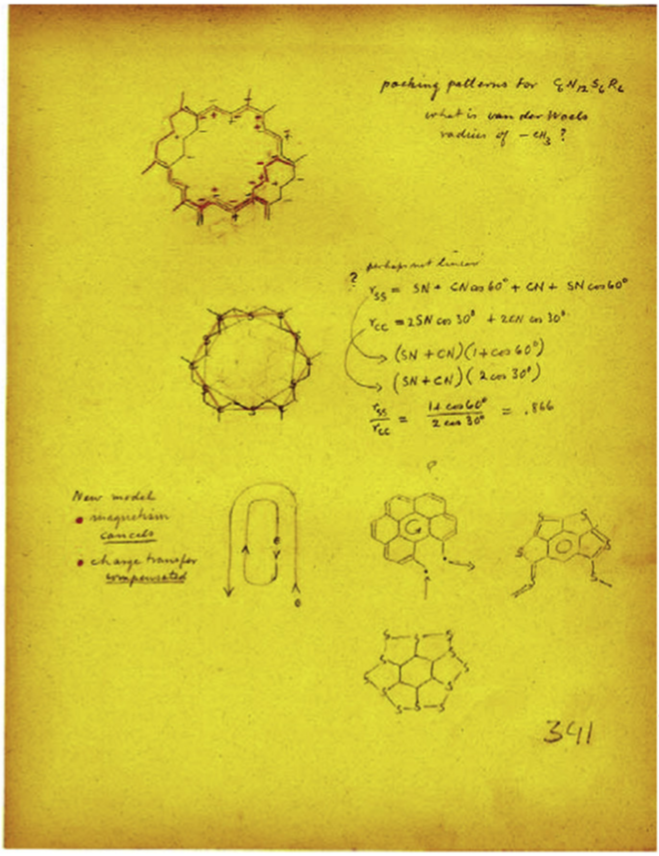


Fig. 16. Networks of the 24-membered heterocycle; RBW notes, p 155, 173, 348, 351, 380.



25

Fig. 17. Alternate network bonding.



packing patterns for $C_6N_{12}S_6R_6$

what is van der Waals radius of $-CH_3$?

perhaps not linear

? $r_{SS} = SN + CN\cos 60° + CN + SN\cos 60°$

$r_{CC} = 2SN\cos 30° + 2CN\cos 30°$

$(SN + CN)(1 + \cos 60°)$

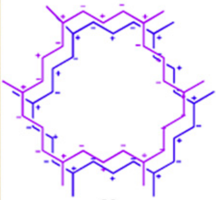
$(SN + CN)(2\cos 30°)$

$\frac{r_{SS}}{r_{CC}} = \frac{1 + \cos 60°}{2\cos 30°} = .866$

?

New model
- magnetism <u>cancels</u>
- charge transfer <u>compensated</u>

341



26

Fig. 18. RBW notes, p 341.

atoms can be calculated; it is near 4.6 Å. Therefore the distance between S_1 and S_4 (diagonal of the hexagon) is approximately 9.2 Å. If one places a benzene ring on the center of the 24-membered ring, the distance been S_1 and the aromatic hydrogen is computed as follows. The distance between H_1 and H_4 in the benzene ring is 2x the C–H bond distance (2.2 Å) plus the C_1–C_4 distance (2.84 Å)= 5.04 Å. Since the S_1–S_4 distance in 9.2 Å, S_1–H_1 and S_4–H_4 are only 2.08 Å apart. This value is considerably less than the sum of the S–H van der Waals radius (1.85+1.1=2.85 Å). Thus a benzene molecule can easily intercalate into the cavity of the 24-membered ring. A ring current can be envisaged to flow across systems, such as **27** subjected to oxidation (Fig. 19).

Hypothetical structure **15** is not known. However in 1988, almost nine years after Woodward's death, a basic seven-membered ring system viz. 1,3,5,2,4,6-trithiatriazepine **28** was synthesized by Rees (**28**, R=H Fig. 20). The seven-membered ring has been shown to undergo nitration and bromination on the single carbon atom. This may afford a route to further manipulation.[20]

In 1985, calculations were carried out on one of the hypothetical components, viz. of trithiatetrazepine in **15**. A literature survey failed to reveal any independent attempt at the synthesis of many of the related structures depicted in **14**–**17** and a related paper describes the synthesis of some new dithiadiazenes and trithiadiazenes derived from *m*-dimercaptobenzene, as shown in Fig. 21.[22]

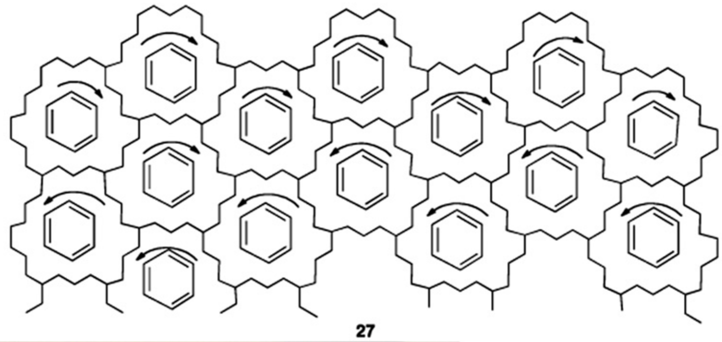
The use of excess *m*-benzenesulfenyl chloride (**32**) led to a red polymeric material in 35% yield (Fig. 22).

The same protocol can now be used to synthesize polymer-related to **18**, using the *p*-disulfenyl chloride (Fig. 23).

Other related, hypothetical molecules conceptualized by RBW are shown in structures **38**–**41** (Fig. 24).

Woodward sketched out a possible synthetic route to such molecules shown below, using the known bis-trimethylsilylsulfurdimide **43** and a pentachloroantimonycyanide complex **42** (Fig. 25).

The resulting diamino derivative **45** can now be reacted with sulfur dichloride to give the heterocycles, **46**, **47**, etc. (Fig. 26).



27

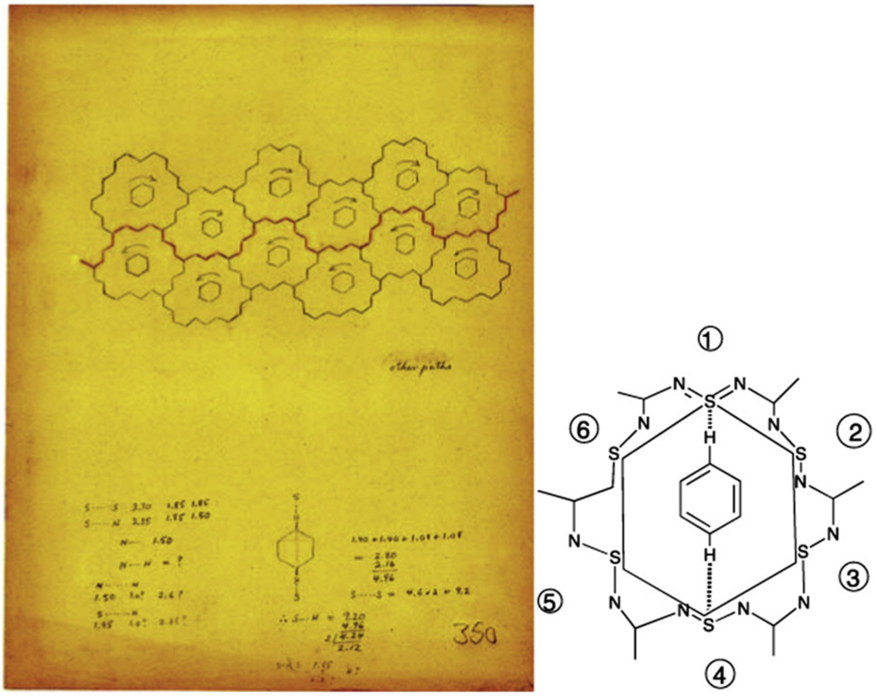
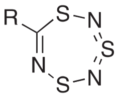


Fig. 19. RBW notes, p 341, 350.



28, R=H; R=NO_2, R=Br

Fig. 20. Heterocycle prepared by Rees.

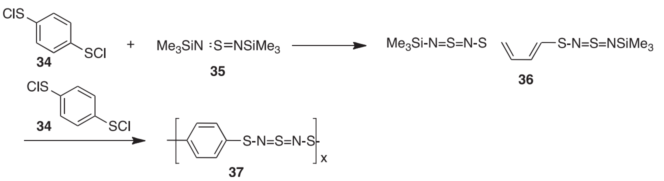


Fig. 23. Some reactions of molecule 34, leading to structure 37.

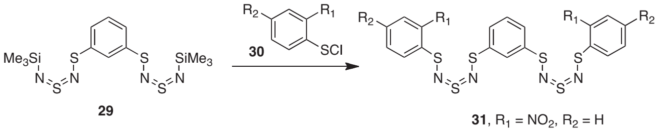


Fig. 21. Dithiadiazenes and trithiadiazenes derived from *m*-dimercaptobenzene (Ref. 22).

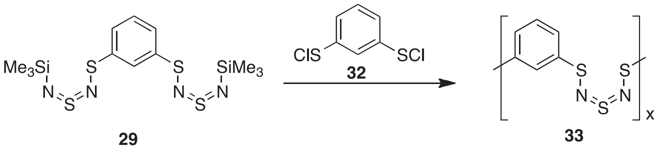
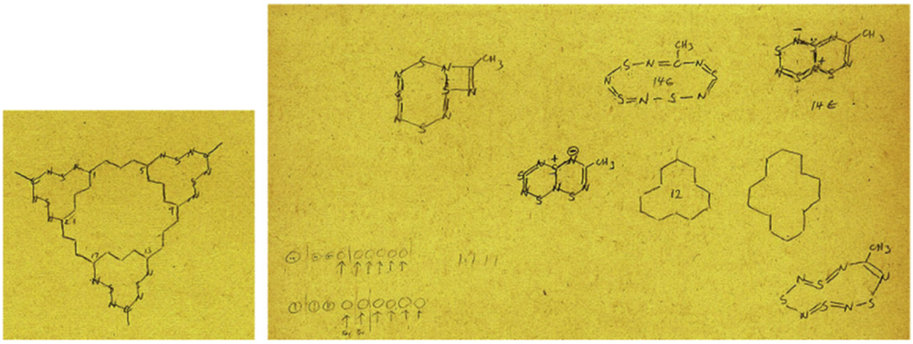
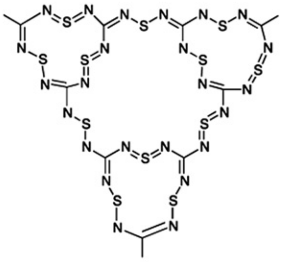


Fig. 22. Structures 29, 32, and 33.

Other interesting variations on the $(SN)_x$ structure are those incorporating triazine and pyrimidine ring systems. These are as yet unknown, but after the death of Woodward other groups have investigated related structures independently. These are discussed next.

A class of polymers referred to as polythiocyanogens have been known for some time, and are denoted by the general formula $S_y(CN)_2$, with Y being an integer.[23,24] All of these entities polymerize very readily in solution and in the solid state to give orange and red products, which are assigned the $[S_y(CN)_2]_x$ formula.[25] As early as 1962, one assignment of the structure of $[S_y(CN)_2]_x$ was based on analogy. Since trimerizes to triazine, these polymers derived from polythiocyanogens were thought to be triazine networks linked by S_y as shown in **48** (Fig. 27).





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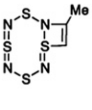

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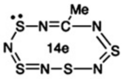

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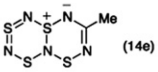
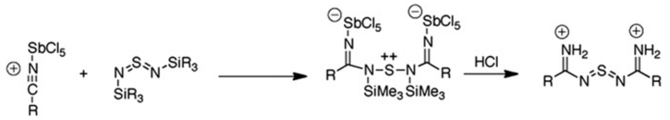


41

Fig. 24. Structure **38** (RBW notes, p 380); **39**–**41** (RBW notes, p 448).



42 **43** **44** **45**

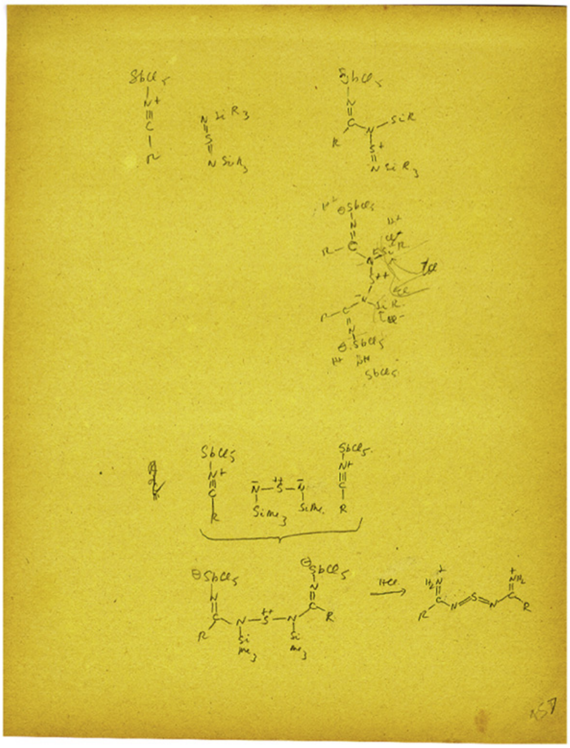
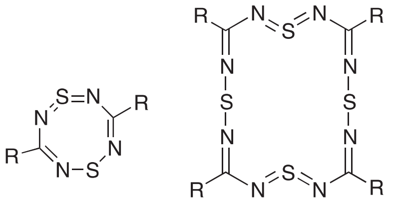
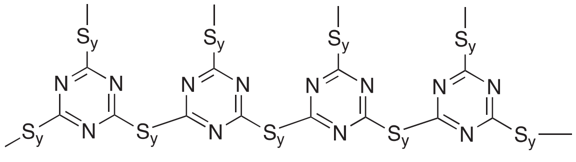


Fig. 25. RBW notes, p 457.



46 **47**

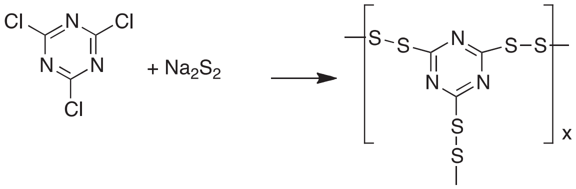
Fig. 26. Structures 46 and 47.



48

Fig. 27. Polymer 48.

More recently, some thiocyanogens were made and their polymerization was studied using FTIR spectroscopy.[25,26] An authentic sample of an oligomer **48** (y=2) was made by reacting trichlorotriazine and disodium disulfide (Fig. 28). This material was not identical to parathiocyanogen derived by either chemical or electrochemical oxidation of thiocyanate anion.

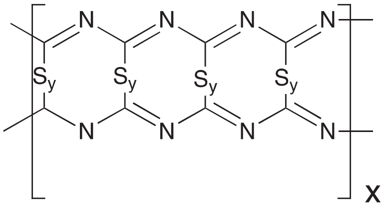


49 **48**

Fig. 28. Polymerization of 49.

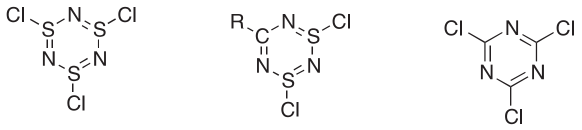
A series of polythiocyanogens $[S_y(CN)_2]$ bearing 1–4 sulfur atoms per unit has been reported. These were assigned structure **50** consisting of two polyazomethine chains bridged by sulfur atoms (Fig. 29).

A related heterocycle, which can be expected to undergo ring-opening polymerization to give SN polymers is **51**. Hybrid molecules **52** and **53** can also be expected to give rise to CN/SN polymers. All of these are known but do not give rise to polymers (Fig. 30).[27]



50

Fig. 29. Polymer 50.



51 **52**, R = t-Bu, Ph, etc. **53**

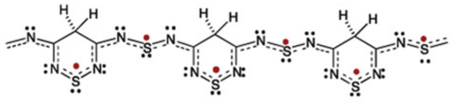
Fig. 30. Molecules 51–53.

Woodward's instinctive feeling was that many of the idealized straight-chain structures written for $(SN)_2$ etc. may not be real led to the following proposal as to what will form an ideal conductor/superconductor. He suggests that a polymer bearing =N–C(R)–N=S constrained in a ring as shown in **54** will allow for free electron flow while preventing kinks in the chain. Note his enthusiastic prediction of an organic superconductor for this structure (Fig. 31).

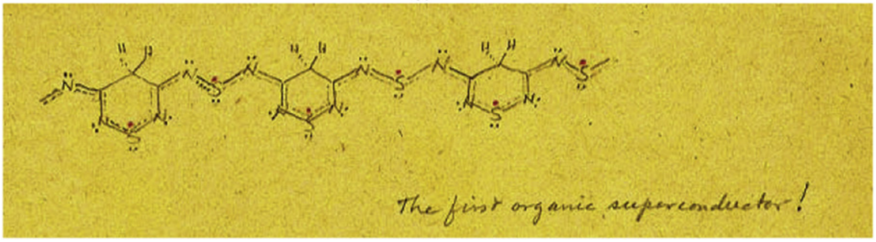
No specific ideas for the synthesis of such a polymer or a potential monomer are elaborated. The authors would like to propose that one needs to synthesize a diamine/diimine attached to a cyclic thiadiaza ring, which on reaction with sulfur dichloride or $SOCl_2$ should give the desired polymer (Fig. 32).

$(RCS)_x$ is a polymer isoelectronic with $(SN)_x$. It has already been seen that $(SN)_x$ is not amenable to modifications to improve its conductivity, stability etc. The one requisite in the hypothetical monomer unit is the presence of an extra unpaired electron in the pi system. The substitution of CR for N opens up the possibility of infinite modifications. In a similar vein, simple molecules isoelectronic with (SN) were considered. The simplest of these is the thioformyl radical HC=S or the thioacyl radical RC=S. Some of the hypothetical polymers built on these group and envisioned by Woodward are shown in Fig. 33.

While these ideas may seem nebulous, one should draw attention to the work carried out by other investigators in this area. For instance a polymeric system analogous to **62** has been studied theoretically by Genin and Hoffmann (Fig. 34).[29]



54



The first organic superconductor!

Fig. 31. Structure **54** (RBW notes, p 364).

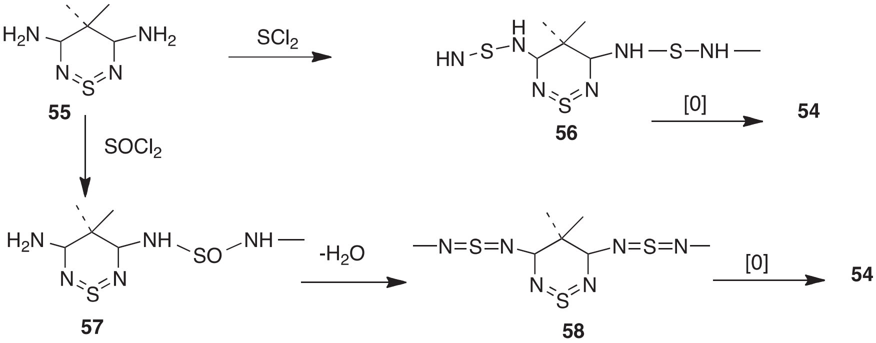


Fig. 32. Author's proposed synthesis of **54**.

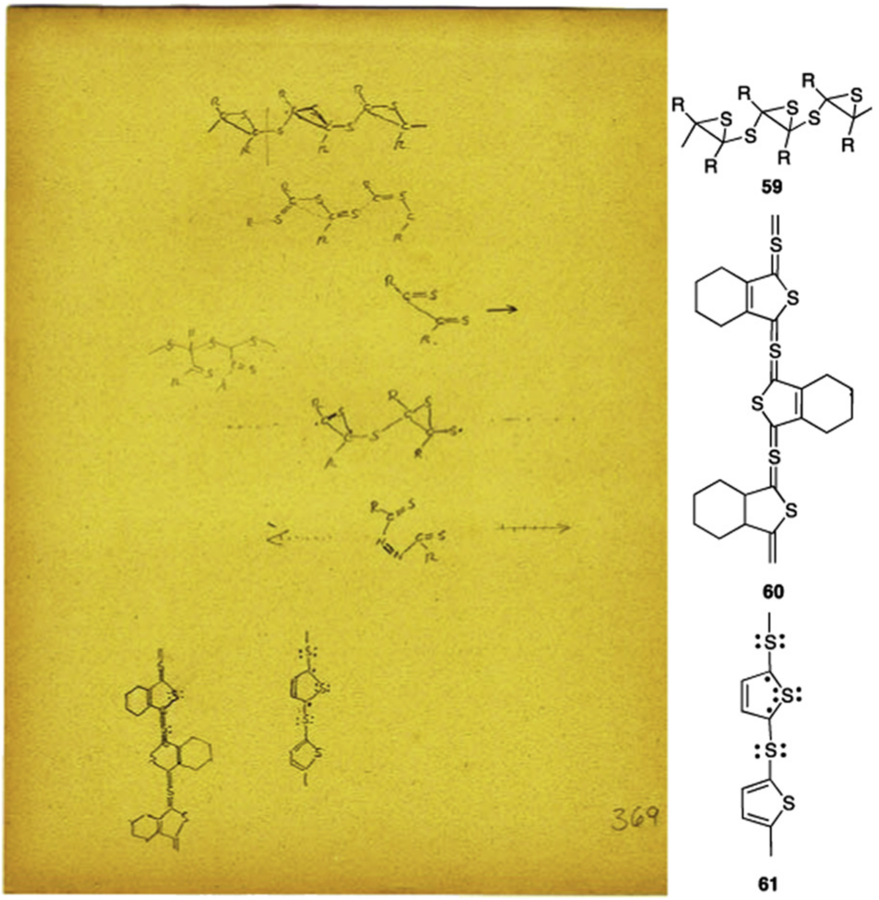


Fig. 33. RBW notes, p 369.

We may also compare and. Polymerization of will give rise to a polymer **65** (Fig. 35) with formally tetravalent sulfur atoms.

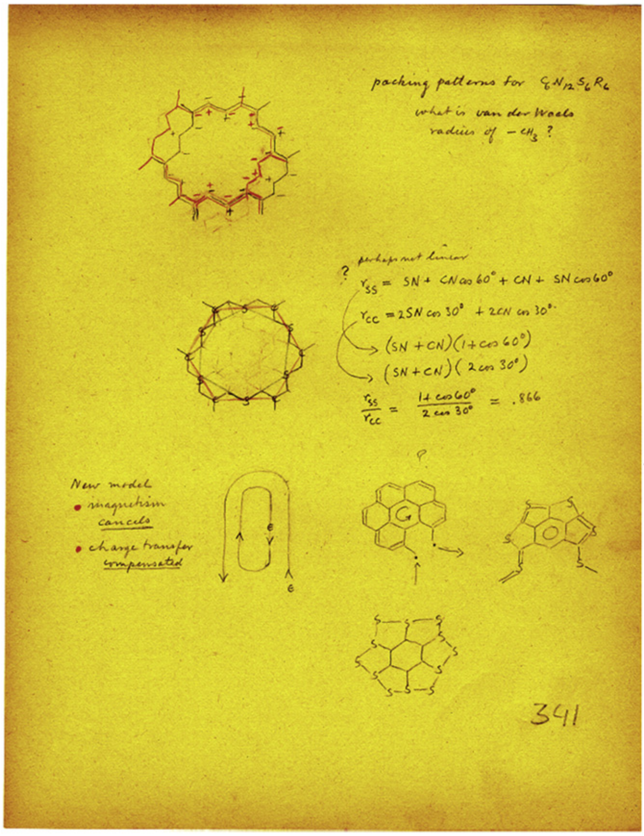
Both Cava and Wudl have worked independently on the thioacyl radical problem. Most interesting is their search for bifunctional RCS systems, such as an *o*-phenylene substituted $(RCS)_x$ shown in **66** (Fig. 36). Polymer **66** can also be viewed as a benzo[*c*]thiophene sulfide polymer.

Wudl's unsuccessful approach involved chloromercuration of benzo[*c*]thiophene followed by treatment with sodium sulfide[28] (Fig. 37).

The Cava approach[30] was based on the unknown benzocyclobutenethione (**69**), and its anticipated inability to undergo electrocylic ring closure to give a benzocyclobutadience dithiete, forcing it to give rise to **66** (Fig. 38).

Suffice it is to say all attempts to generate benzocyclobutenedithione or other vicinal dithiones did not succeed. These results are detailed in a thesis submitted by M. Levinson to the University of Pennsylvania in 1984.[30]

Yet another precursor envisioned by Woodward, viz. trithiophthalic anhydride, is unknown. This has been an ongoing independent research area in the Cava group. Recently there have been unsubstantiated claims to its synthesis.[31] Thiophthalic anhydride **75**, thionothiophthalic anhydride (**76**) are well characterized but not the trithioanhydride **77**.[32]



packing patterns for $C_6N_{12}S_6R_6$

what is van der Waals radius of $-CH_3$?

perhaps not linear

?

r_{SS} = SN + CN cos 60° + CN + SN cos 60°

r_{CC} = 2SN cos 30° + 2CN cos 30°.

$\rightarrow$ (SN + CN)(1 + cos 60°)

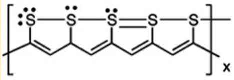
$\rightarrow$ (SN + CN)(2 cos 30°)

$\frac{r_{SS}}{r_{CC}} = \frac{1 + \cos 60°}{2 \cos 30°} = .866$

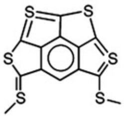
New model

- magnetism cancels
- charge transfer compensated

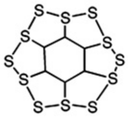
341



62



63

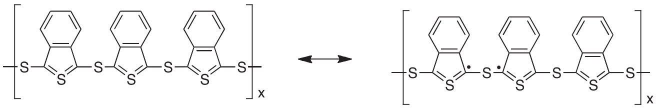


64

Fig. 34. RBW notes, p 341.

65

Fig. 35. Two resonance structures for 65.



66

Fig. 36. Resonance structures for 66.

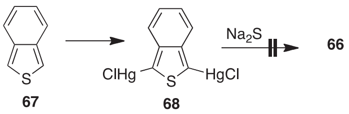


Fig. 37. Reactions of 67.

Interestingly enough, the 2,3-naphthalene analog **78** has been made and found to be stable. The difference has been ascribed to the greater contribution of a diradical structure in **77** compared to **78** (Fig. 39).[33]

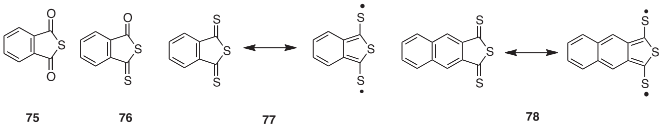


Fig. 39.

In addition, Woodward's unpublished notes contain ideas on TTF oligomers, organometallic derivatives, and many other beautiful structures. Some of these are displayed in the remaining figures and have no text annotation to explain their origin or context with respect to the current chemical literature. It is indeed our hope that the entire set of scanned images of the RBW notes will be made available to the chemical community as other chemists and theoreticians working in this area might be further stimulated by R. B. Woodward's remarkable imagination and depth of thought. For this remarkable organic chemist's fecund imagination thought up molecules that even now have immense interest and potential for our science Figs. 40–56.

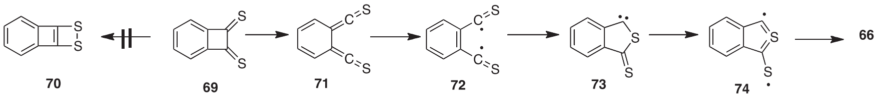


Fig. 38. Cava approach to polymer **66**.

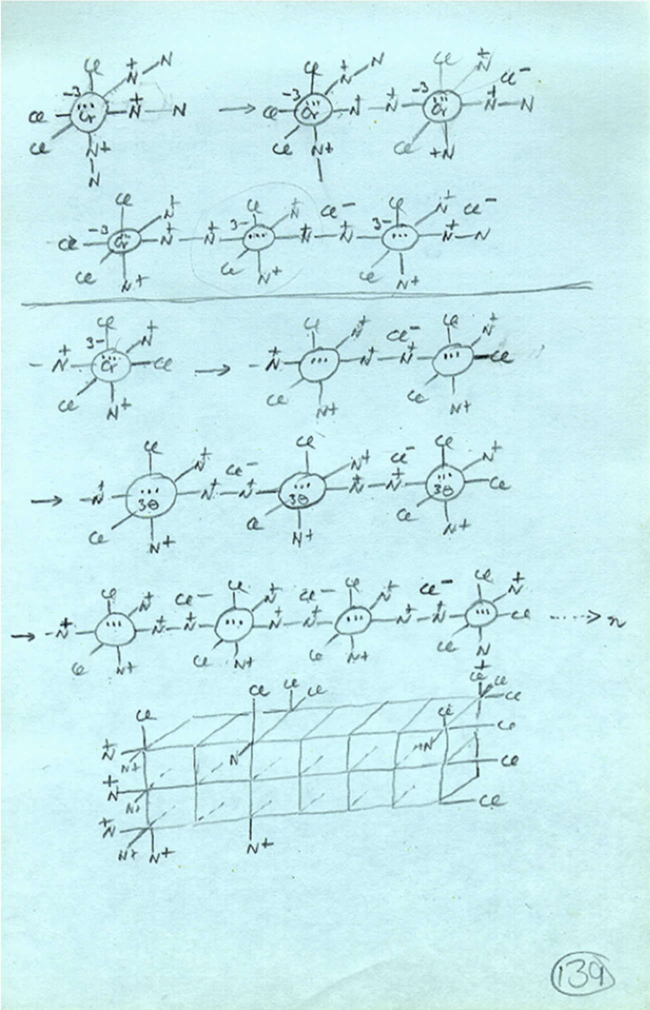
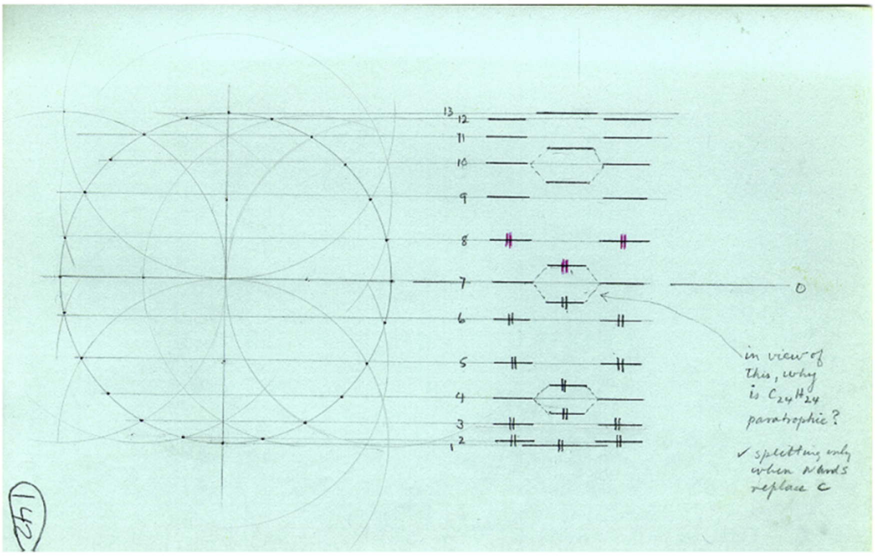


Fig. 40. RBW notes, p 139.



in view of this, why is $C_{24}H_{24}$ paratrophic?

✓ splitting only when N and S replace C

Fig. 41. RBW notes, p 142.

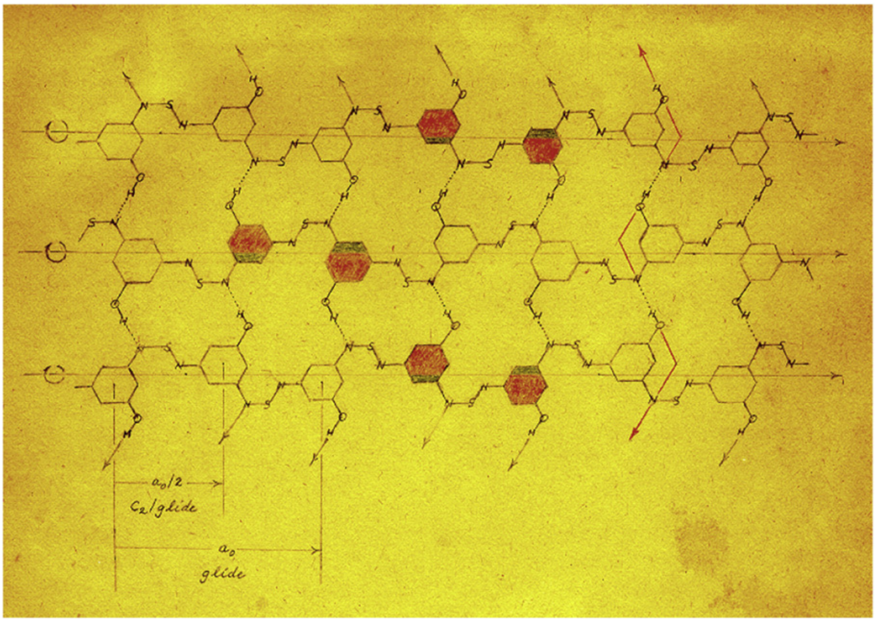


Fig. 42. RBW notes, p 174.

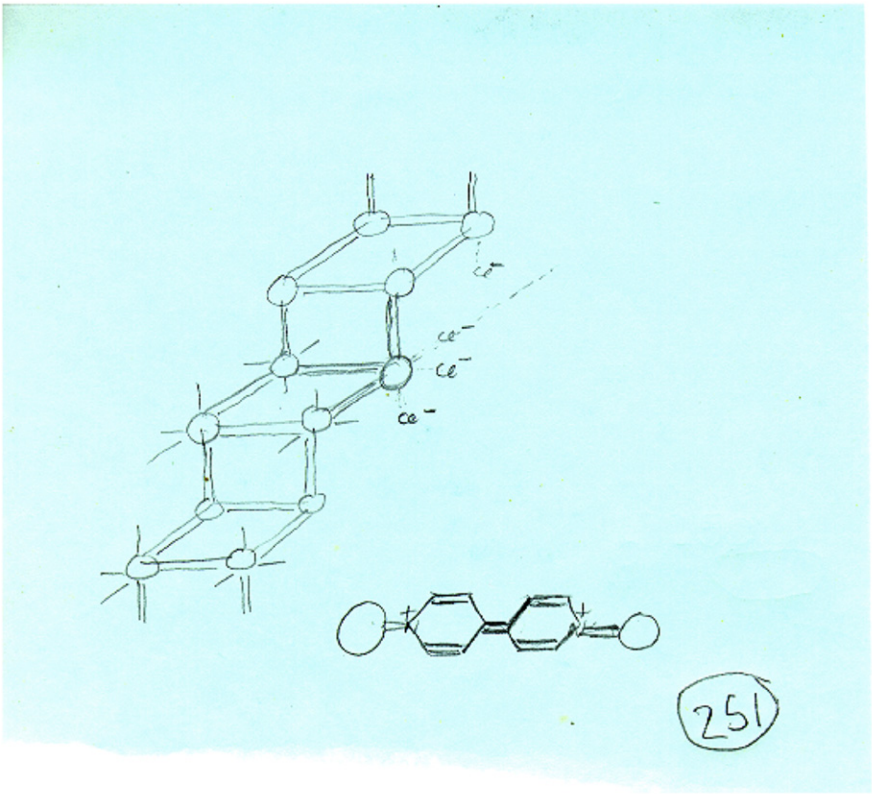
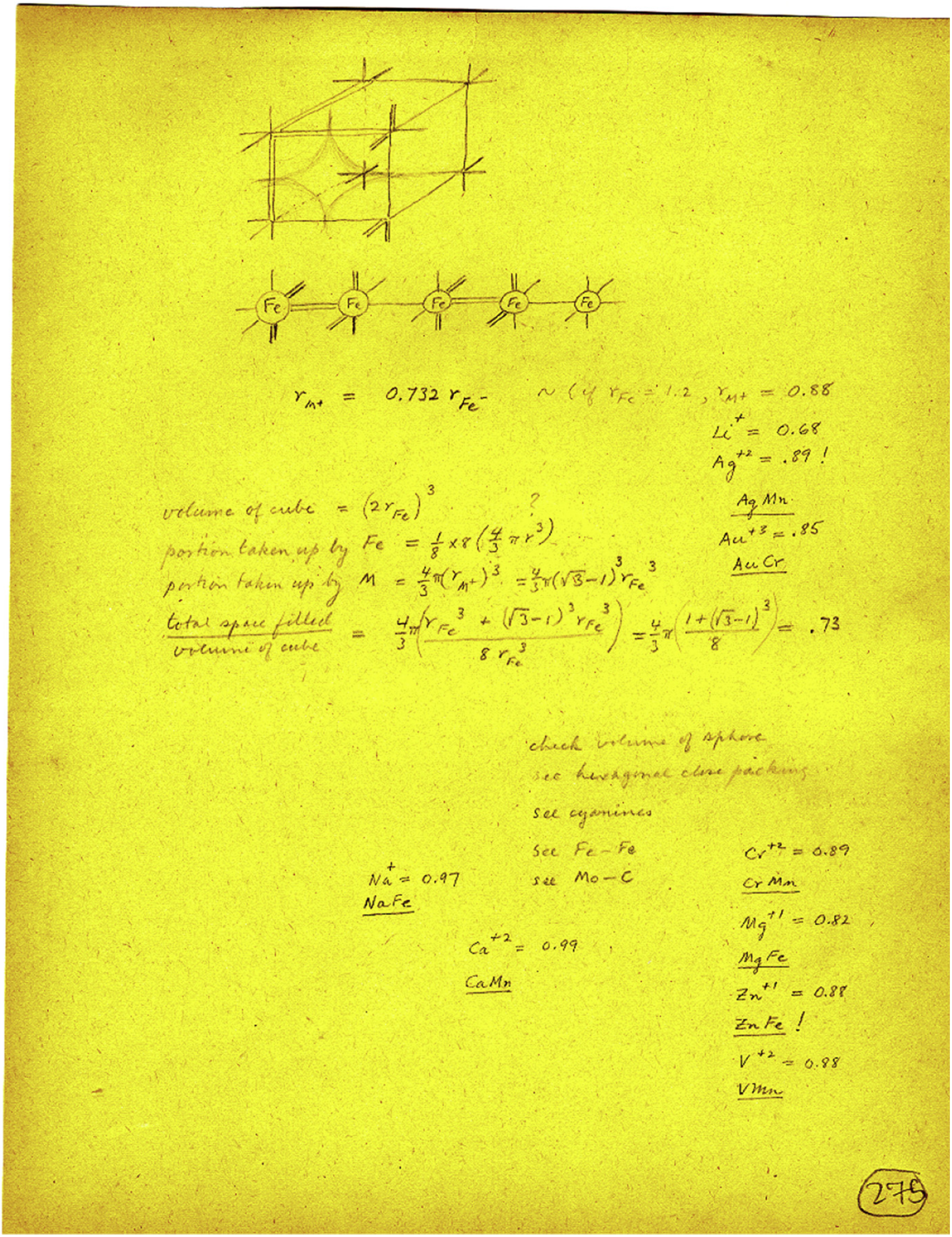


Fig. 43. RBW notes, p 251.



$r_{M^+} = 0.732\, r_{Fe^-}$ $\sim$ (if $r_{Fe} = 1.2$, $r_{M^+} = 0.88$

$Li^+ = 0.68$

$Ag^{+2} = .89$!

$\underline{AgMn}$

$Au^{+3} = .85$

$\underline{AuCr}$

volume of cube $= (2r_{Fe})^3$?

portion taken up by Fe $= \frac{1}{8} \times 8 \left(\frac{4}{3}\pi r^3\right)$

portion taken up by M $= \frac{4}{3}\pi (r_{M^+})^3 = \frac{4}{3}\pi(\sqrt{3}-1)^3 r_{Fe}^3$

$$\frac{\text{total space filled}}{\text{volume of cube}} = \frac{4}{3}\pi\left(\frac{r_{Fe}^3 + (\sqrt{3}-1)^3 r_{Fe}^3}{8 r_{Fe}^3}\right) = \frac{4}{3}\pi\left(\frac{1+(\sqrt{3}-1)^3}{8}\right) = .73$$

check volume of sphere

see hexaginal close packing

see cyanines

see Fe–Fe

see Mo–C

$Cr^{+2} = 0.89$

$\underline{CrMn}$

$Na^+ = 0.97$

$\underline{NaFe}$

$Mg^{+1} = 0.82$

$\underline{MgFe}$

$Ca^{+2} = 0.99$

$\underline{CaMn}$

$Zn^{+1} = 0.88$

$\underline{ZnFe}$!

$V^{+2} = 0.88$

$\underline{VMn}$

275

Fig. 44. RBW notes, p 275.

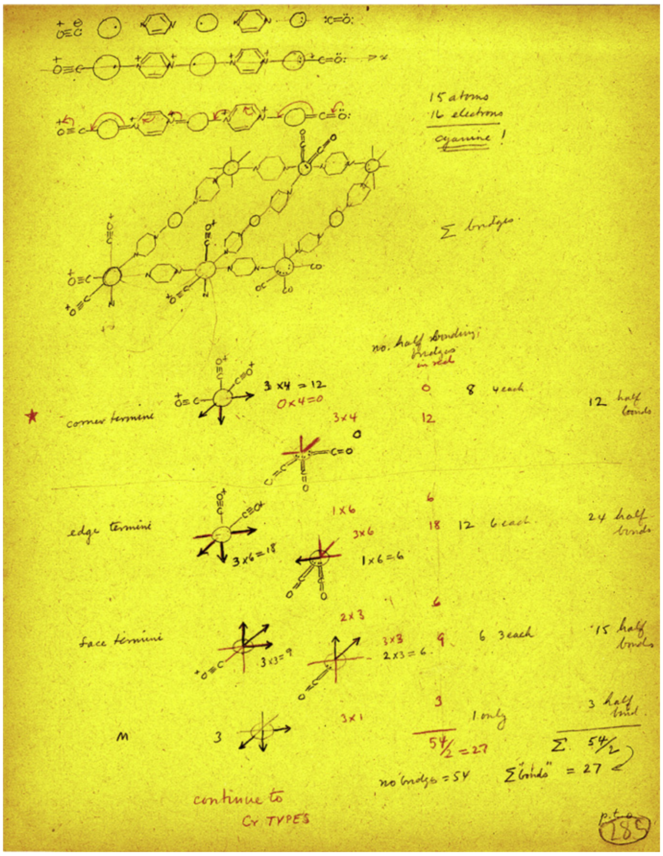


Fig. 45. RBW notes, p 285.

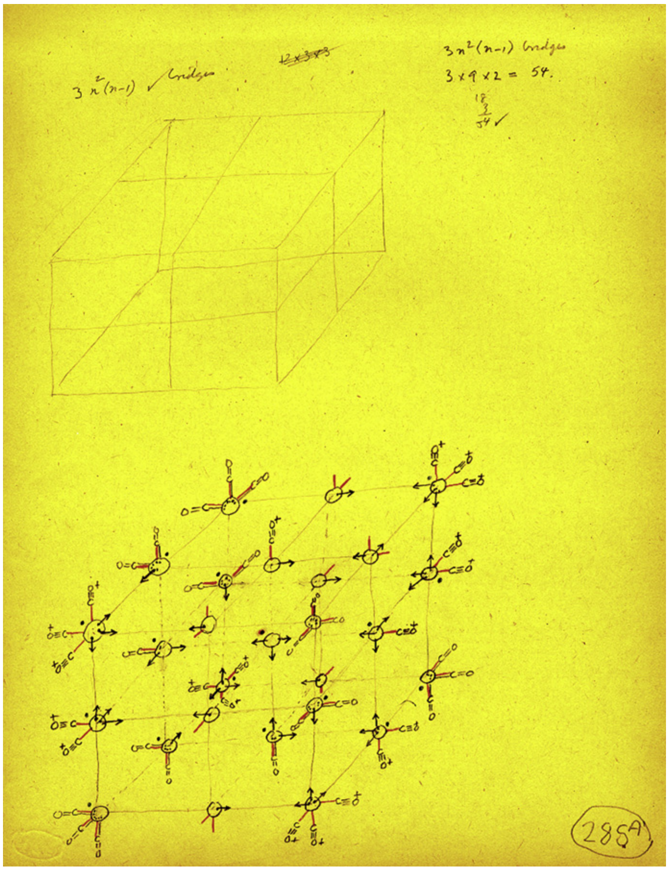
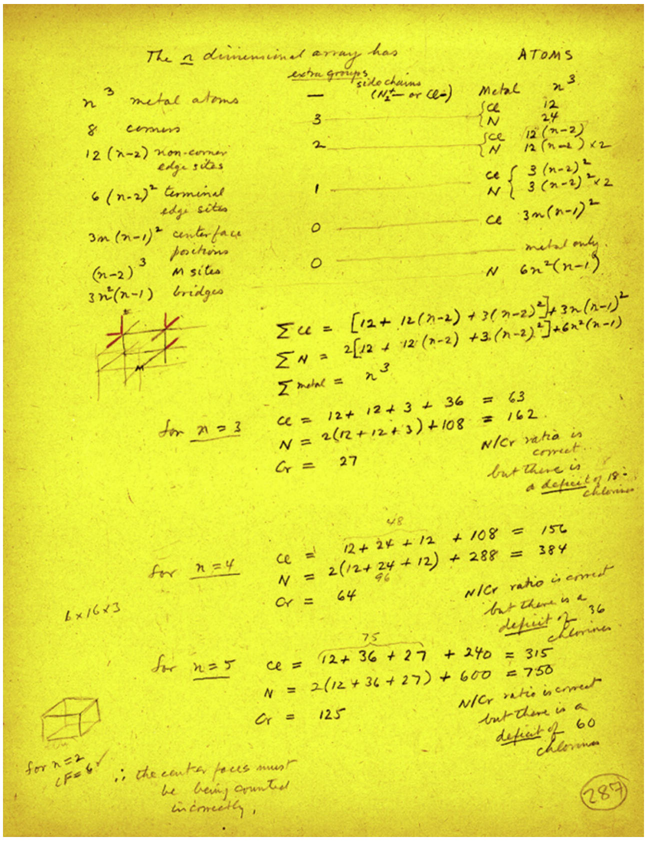


Fig. 46. RBW notes, p 285A.



The n dimensional array has	extra groups side chains (N_2^+ or Cl−)	ATOMS
n^3 metal atoms	—	Metal n^3
8 corners	3	Cl 12 N 24
$12(n-2)$ non-corner edge sites	2	Cl $12(n-2)$ N $12(n-2)\times 2$
$6(n-2)^2$ terminal edge sites	1	Cl $3(n-2)^2$ N $3(n-2)^2\times 2$
$3n(n-1)^2$ center face positions	0	Cl $3n(n-1)^2$
$(n-2)^3$ M sites	0	metal only
$3n^2(n-1)$ bridges		N $6n^2(n-1)$

$$\sum Cl = [12 + 12(n-2) + 3(n-2)^2] + 3n(n-1)^2$$
$$\sum N = 2[12 + 12(n-2) + 3(n-2)^2] + 6n^2(n-1)$$
$$\sum \text{metal} = n^3$$

for $n = 3$

$$Cl = 12 + 12 + 3 + 36 = 63$$
$$N = 2(12+12+3) + 108 = 162$$
$$Cr = 27$$

N/Cr ratio is correct but there is a deficit of 18 chlorines

for $n = 4$

$$Cl = \overbrace{12 + 24 + 12}^{48} + 108 = 156$$
$$N = 2(12 + \underset{96}{24} + 12) + 288 = 384$$
$$Cr = 64$$

$6\times16\times3$

N/Cr ratio is correct but there is a deficit of 36 chlorines

for $n = 5$

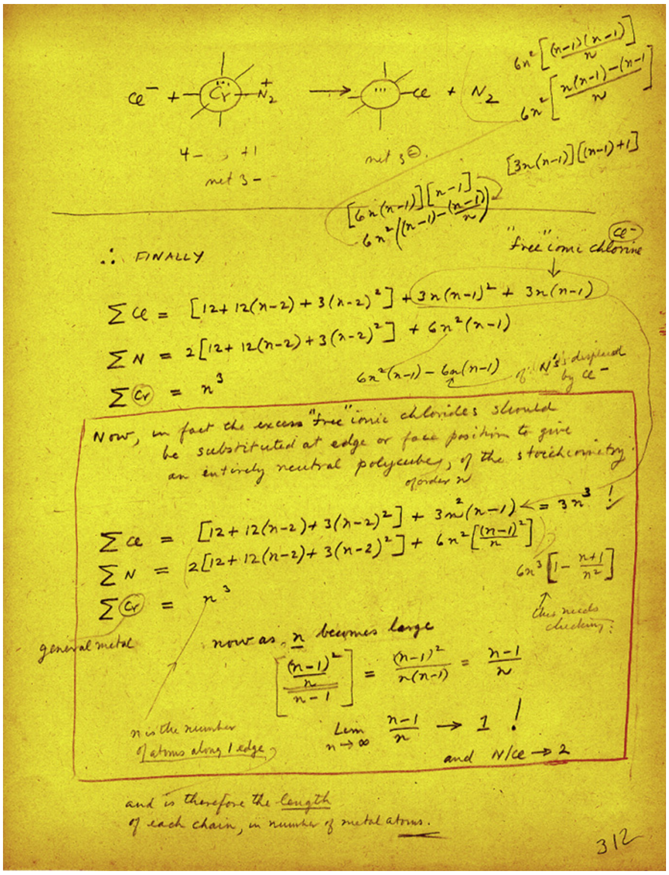
$$Cl = \overbrace{12 + 36 + 27}^{75} + 240 = 315$$
$$N = 2(12 + 36 + 27) + 600 = 750$$
$$Cr = 125$$

N/Cr ratio is correct but there is a deficit of 60 chlorines

for $n=2$ CF = 6 ✓ ∴ the center faces must be being counted incorrectly.

(287)

Fig. 47. RBW notes, p 287.



Cl^- + Cr $\overset{+}{N_2}$ → Cl + N_2

4− , +1 net 3−

net 3⊖

$$6n^2\left[\frac{(n-1)(n-1)}{n}\right]$$
$$6n^2\left[\frac{n(n-1)-(n-1)}{n}\right]$$
$$[3n(n-1)][(n-1)+1]$$
$$[6n(n-1)][n-1]$$
$$6n^2\left((n-1)-\frac{(n-1)}{n}\right)$$

∴ FINALLY

"free" ionic chlorine (Cl^-)

$$\sum Cl = [12 + 12(n-2) + 3(n-2)^2] + 3n(n-1)^2 + 3n(n-1)$$
$$\sum N = 2[12 + 12(n-2) + 3(n-2)^2] + 6n^2(n-1)$$
$$6n^2(n-1) - 6n(n-1)$$

N's displaced by Cl^-

$$\sum Cr = n^3$$

Now, in fact the excess "free" ionic chlorides should be substituted at edge or face position to give an entirely neutral polycube, of the stoichiometry of order n

$$\sum Cl = [12 + 12(n-2) + 3(n-2)^2] + 3n^2(n-1) \leftarrow = 3n^3 \ !$$
$$\sum N = 2[12 + 12(n-2) + 3(n-2)^2] + 6n^2\left[\frac{(n-1)^2}{n}\right]$$
$$6n^3\left[1-\frac{n+1}{n^2}\right]$$

this needs checking:

$$\sum Cr = n^3$$

general metal

now as n becomes large

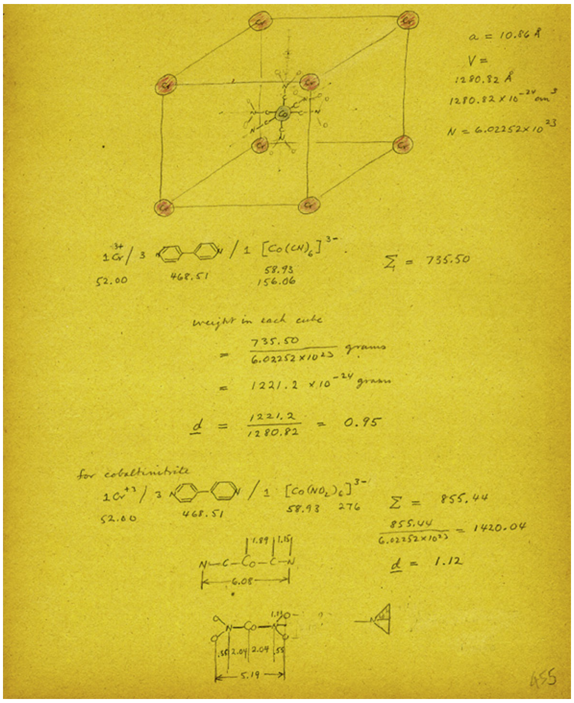
$$\left[\frac{\frac{(n-1)^2}{n}}{n-1}\right] = \frac{(n-1)^2}{n(n-1)} = \frac{n-1}{n}$$
$$\lim_{n\to\infty} \frac{n-1}{n} \to 1 \ !$$

and N/Cl → 2

n is the number of atoms along 1 edge, and is therefore the length of each chain, in number of metal atoms.

312

Fig. 48. RBW notes, p 312.



$a = 10.86$ Å

$V =$

1280.82 Å

1280.82×10^{-24} cm^3

$N = 6.02252 \times 10^{23}$

$1\overset{3+}{\text{Cr}} / 3$ [structure] $/ 1\ [\text{Co(CN)}_6]^{3-}$.

52.00 468.51 58.93 156.06

$\Sigma = 735.50$

weight in each cube

$= \frac{735.50}{6.02252 \times 10^{23}}$ grams

$= 1221.2 \times 10^{-24}$ grams

$\underline{d} = \frac{1221.2}{1280.82} = 0.95$

for cobaltinitrite

$1\text{Cr}^{+3} / 3$ [structure] $/ 1\ [\text{Co(NO}_2)_6]^{3-}$

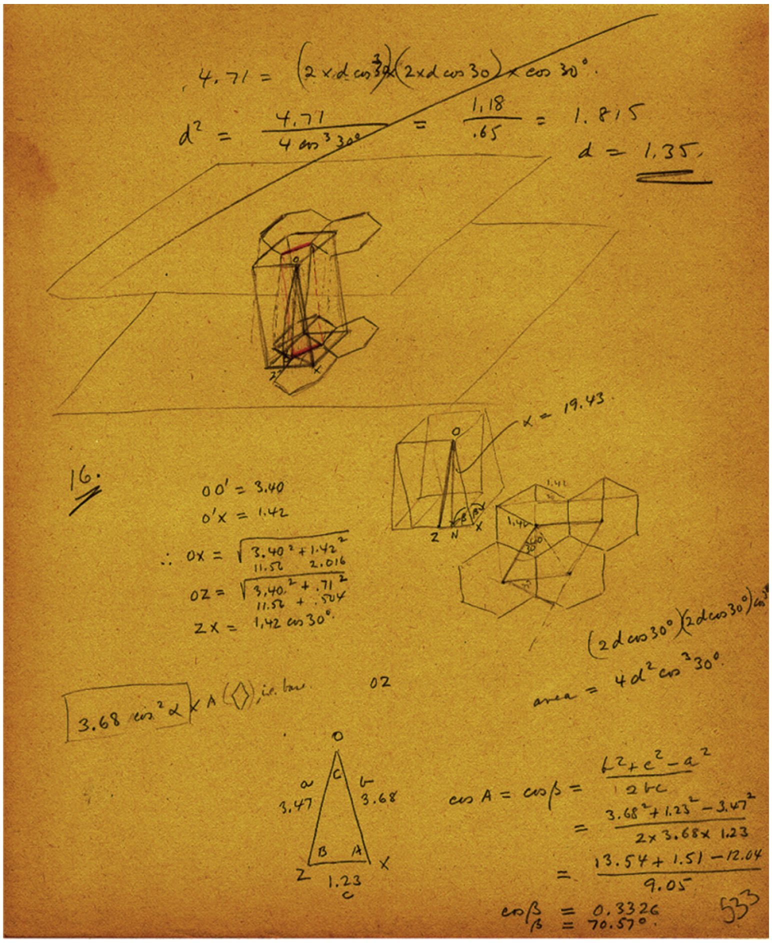
52.00 468.51 58.93 276

$\Sigma = 855.44$

$\frac{855.44}{6.02252 \times 10^{23}} = 1420.04$

$\underline{d} = 1.12$

Fig. 49. RBW notes, p 455.



$4.71 = (2 \times d \cos 30)(2 \times d \cos 30) \times \cos 30°$.

$d^2 = \frac{4.71}{4 \cos^3 30°} = \frac{1.18}{.65} = 1.815$

$d = \underline{\underline{1.35}}$

$x = 19.43$.

16.

$OO' = 3.40$

$O'X = 1.42$

$\therefore OX = \sqrt{3.40^2 + 1.42^2}$ 11.56 2.016

$OZ = \sqrt{3.40^2 + .71^2}$ 11.56 + .504

$ZX = 1.42 \cos 30°$.

$\boxed{3.68 \cos^2 \alpha} \times A(\lozenge)$, i.e. [illegible]

OZ

$(2d \cos 30°)(2d \cos 30°) \cos 30°$

area $= 4d^2 \cos^3 30°$

$\cos A = \cos\beta = \frac{b^2 + c^2 - a^2}{2bc}$

$= \frac{3.68^2 + 1.23^2 - 3.47^2}{2 \times 3.68 \times 1.23}$

$= \frac{13.54 + 1.51 - 12.04}{9.05}$

$\cos\beta = 0.3326$

$\beta = 70.57°$.

Fig. 50. RBW notes, p 533.

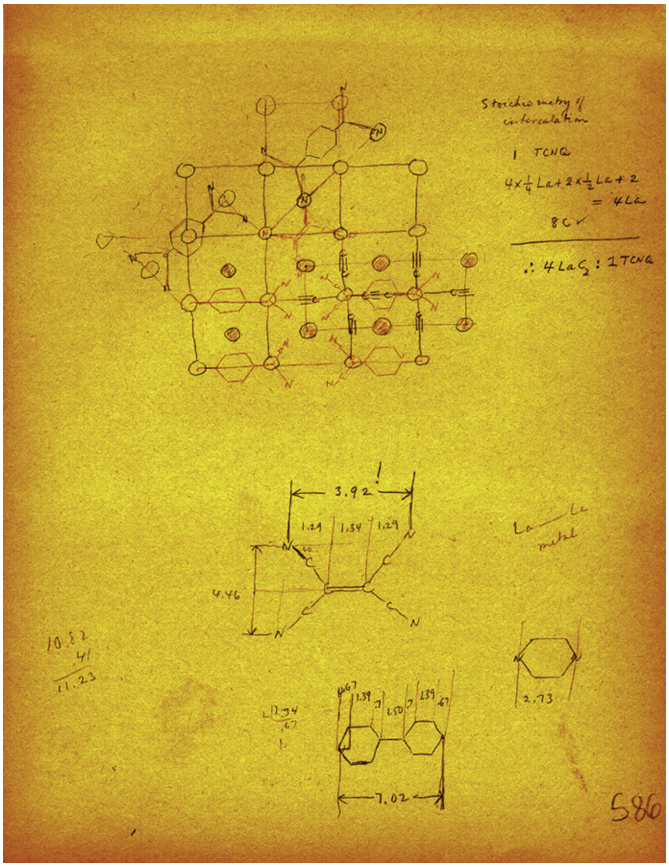


Fig. 51. RBW notes, p 586.

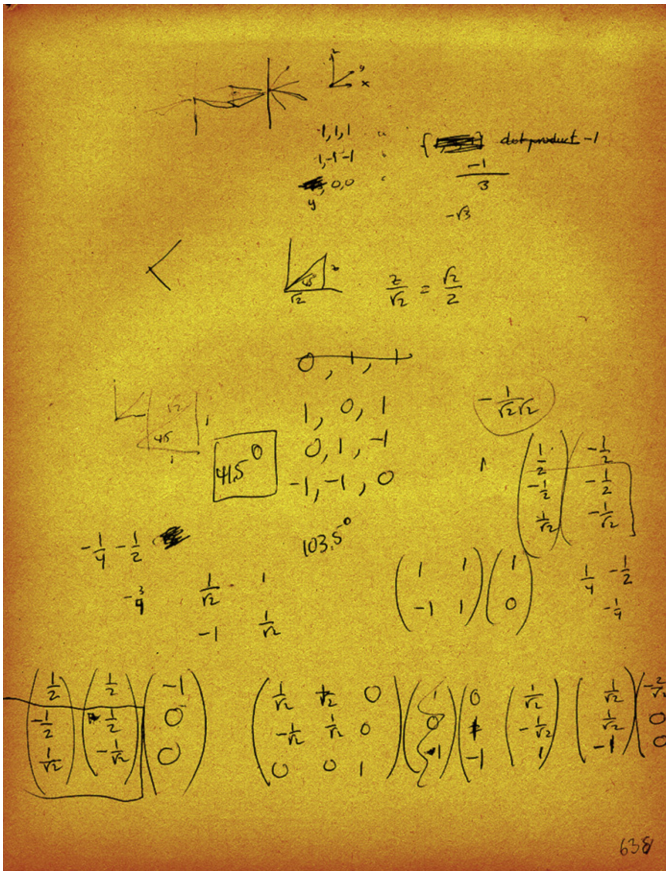


Fig. 52. RBW notes, p 638. This page clearly of lower quality than other pages, and in a different hand, is actually by Roald Hoffmann. It came out of their mutual discussions in the course of the research.

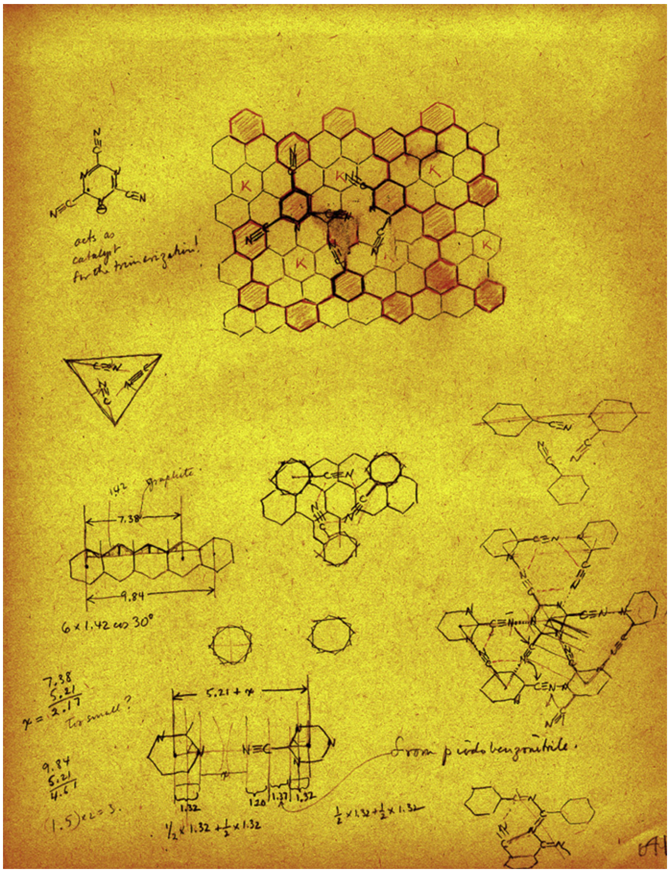


Fig. 53. RBW notes, p 641.

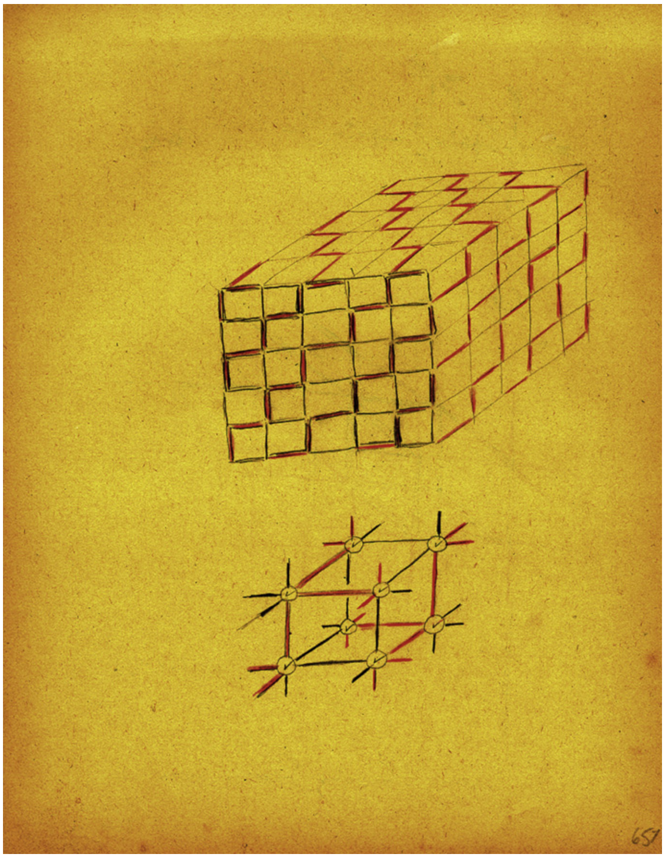
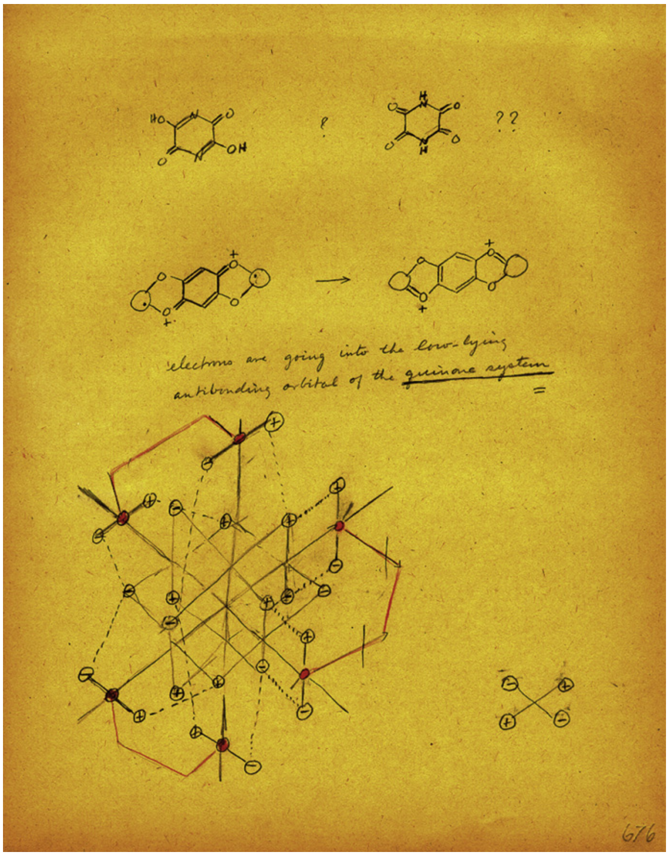
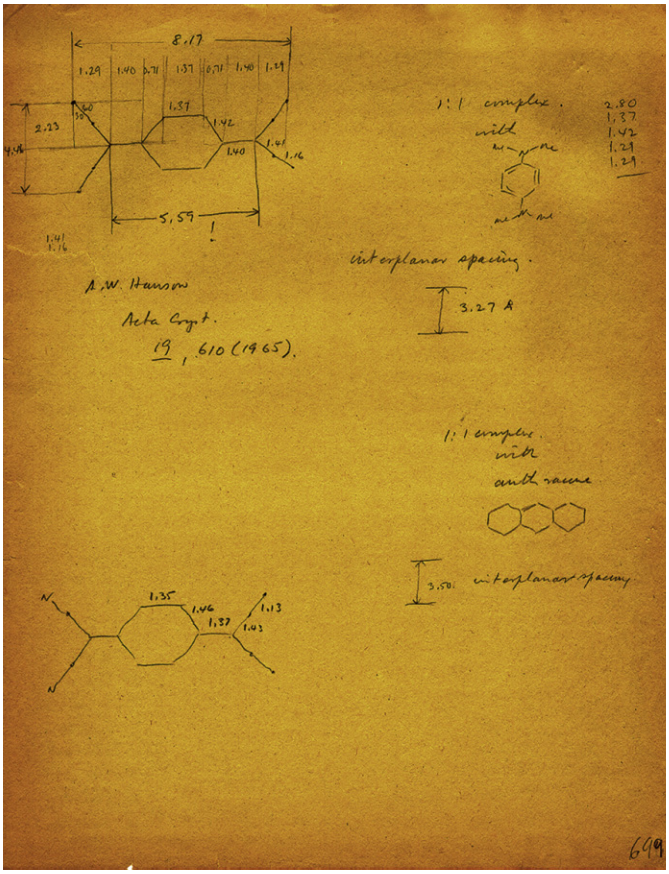


Fig. 54. RBW notes, p 657.



electrons are going into the low-lying antibonding orbital of the quinone system

Fig. 55. RBW notes, p 676.



1:1 complex. with

interplanar spacing.

A.W. Hanson

Acta Cryst. 19, 610 (1965).

1:1 complex. with anthracene

3.50 interplanar spacing

Fig. 56. RBW notes, p 699; the last page.

Acknowledgements

MPC and MVL wish to thank Prof. Robert M. Williams, Colorado State University for getting us involved in this challenging project. All of the authors wish to express their sincere gratitude to Mr. Eric Woodward and Ms. Crystal Woodward who made their father's notes available to us. Support from the National Science Foundation (Che-9901177 to MPC) is gratefully acknowledged. The authors are deeply indebted to Prof. Fred Wudl, of the University of California, Santa Barbara, for careful reading of the manuscript and helpful suggestions.

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Biographical sketch

Roald Hoffmann was born in 1937 in Złoczów, Poland. Having survived the war, he came to the U. S. in 1949, and studied chemistry at Columbia and Harvard Universities (Ph.D. 1962). Since 1965 he is at Cornell University, now as the Frank H. T. Rhodes Professor of Humane Letters, Emeritus. He has received many of the honors of his profession, including the 1981 Nobel Prize in Chemistry (shared with Kenichi Fukui). Had R.B.W. lived, he most surely would have shared in that award. Active also as a writer, Hoffmann has carved out his own land 'twixt science, poetry, and philosophy, through many essays and several books of poetry, plays, and nonfiction.

Robert M. Williams was born in New York in 1953 and received the B.A. degree in Chemistry in 1975 from Syracuse University (Ei-ichi Negishi). He obtained the Ph.D. degree in 1979 at MIT (W.H. Rastetter) and was a post-doctoral fellow at Harvard (1979–1980; R.B. Woodward/Yoshito Kishi). He joined Colorado State University in 1980 and was named a University Distinguished Professor in 2002. He has won several awards including the ACS Arthur C. Cope Scholar Award (2002) and the ACS Ernest Guenther Award in the Chemistry of Natural Products (2011). His interdisciplinary research program at the chemistry–biology interface is focused on the total synthesis of biomedically significant natural products, biosynthesis of secondary metabolites, studies on antitumor drug-DNA interactions, HDAC inhibitors, amino acids, and peptides.