Thermal Behavior of Diynes with Formally Conjugated Heteroaromatic Sidegroups

Abhijit Sarkar[*,#] **and Satya S. Talwar**

Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400076, India

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Diynes with heteroaromatic sidegroups directly linked to the acetylenic backbone were found to show liquid crystalline behaviour upon heating. Thus, 1,4-di(2-thienyl)-1,3-butadiyne, 1,4-di(3-thienyl)-1,3-butadiyne, 1,4-di(3-benzo[*b*]thienyl)-1,3-butadiyne, 1-(3-quinolyl)-4-(2-thienyl)-1,3-butadiyne, 1-(3-quinolyl)-4-(3-thienyl)-1,3-butadiyne, and 5-(2-thienyl)-2,4-pentadiyne-1-ol were investigated for their thermal behavior. These diynes also underwent polymerization in their liquid crystalline state, although the polymers so formed did not show liquid crystalline behavior. It was found that the S-atom of the heteroaromatic moieties tends to play a role in making the diynes show liquid crystalline behavior. Differential scanning calorimetry, thermogravimetric analysis and hot stage microscopy were used to investigate the liquid crystalline nature of the diynes. All of them showed a nematic liquid crystalline phase upon annealing, whereas smectic phase was totally absent.

The 1,4-disubstituted 1,3-butadiynes have been mainly investigated as regards their solid state polymerization. Many of these monomers undergo solid state 1,4-addition polymerization wherein the reactivity of the diynes is topochemically controlled.[1—4] However, the structural similarity of diphenylbutadiyne to the well-known tolane liquid crystals have drawn the attention of investigators since the late seventies.[5—7] The rigid rod-like structure of diphenylbutadiyne meets the requirements for liquid crystallinity. Grant reported the first example of liquid crystalline materials possessing a diacetylene nucleus,[6] the compounds being 1,4-bis(4-*n*-acyloxyphenyl)-1,3-butadiyne series and 1-(4-*n*-alkoxyphenyl)-4-(4-cyanophenyl)-1,3-butadiyne series. Several interesting inferences were drawn from the thermal studies of the above two series. All of them displayed a nematic liquid crystalline phase. Smectic behavior was not observed in any of these compounds. The mesomeric behavior of rigid rod-like organic molecules has been of great interest for application to various information display technologies.

The divinylbutadiyne (DVBY) (1,7-Octadiene-3,5-diyne) monomers crystallize at low temperatures as mesogenic crystals in which the long molecular axes of the DVBY molecules are all aligned along a single direction of a monoclinic unit cell. Such structures are considered as low temperature precursors to high temperature liquid crystalline state. The first case of mesogenic disubstituted divinylbutadiyne (DVBY) monomers that form thermotropic liquid crystal phases was reported by Garito et al.[8] wherein the monomers underwent liquid crystal polymerization on thermal annealing to yield highly conjugated liquid crystalline polymers. From third harmonic generation studies in the near infrared region, centrosymmetric DVBY liquid crystals and liquid crystal polymers have been shown to possess third order nonlinear susceptibilities, $\chi^{(3)}$ two orders of magnitude larger than quartz. Their intensity dependent indices of refraction were comparable to those of germanium.[9,10]

In search of new materials exhibiting nonlinear optical properties, many scientists have studied conjugated systems bearing a donor group at one end and an acceptor group at the other end.[9,11—13] As non-centrosymmetric and highly polarizable molecules, these are likely to yield materials displaying large macroscopic optical nonlinearity. The physical properties may be expected to be enhanced further, if these molecules are incorporated into organized supramolecular arrangements such as liquid crystals. Fouquey et al. reported such type of molecules where mesophases were formed by push-pull stilbenes and butadiynes.[12]

Milburn et al. have investigated a series of butadiynes which show thermotropic liquid crystalline behavior.[14—16] One of the various classes which has been investigated by them is the Schiff's bases attached to butadiyne molecules. Almost all the compounds investigated by Milburn et al. polymerized in liquid crystalline state. It was observed that unsymmetrically substituted diynes often exist in smectic and nematic mesophases which polymerize in the liquid crystalline state, whereas the incorporation of diyne into potentially liquid crystalline material does not always lead to liquid crystalline polymers. The monomers of these materials are sometimes $\chi^{(2)}$ active, but the polymers are not. Further, it was inferred that the polymerization in the liquid crystalline state may have proceeded by an alternative route other than the 1,4-addition polymerization.

As part of our investigation on diynes containing conjugated heteroaromatic side groups, we have done thermal studies of the monomers **1**, **2**, **3**, **4**, **5**, and **6** (Fig. 1). An

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[#] Present address: Institute for Chemical Reaction Science, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.

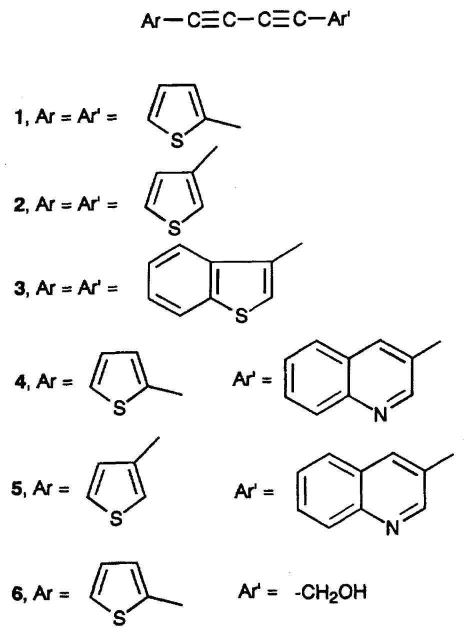


Fig. 1. Molecular structures of diynes discussed in this paper.

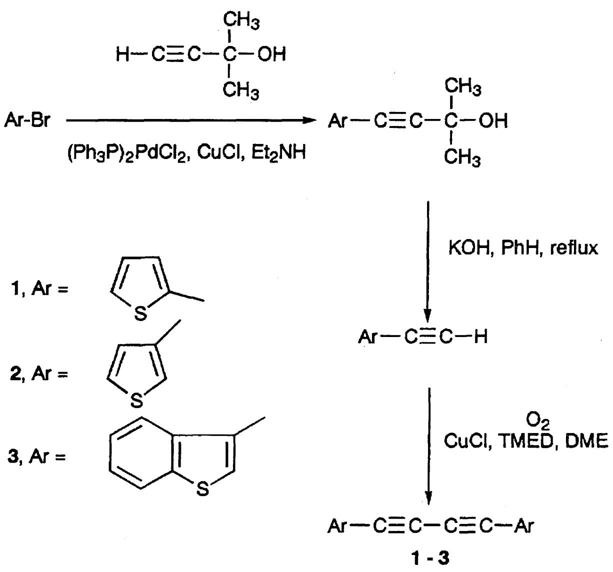
interesting and novel thermal behavior was observed during these studies for all the above diynes. Crystals of these monomers, upon heating, were found to undergo a transition to translucent phase which slowly polymerized upon continued heating. There is no previous report on liquid crystalline behavior of diynes with heteroaromatic sidegroups. In this sense, our studies acquire added significance and novelty. Although the ultimate goal of this work is based on the idea of combining liquid crystalline properties with the conjugation-related properties of polyynes which may lead to the development of materials with better nonlinear optical properties, this investigation centers around more basic aspects.

Experimental

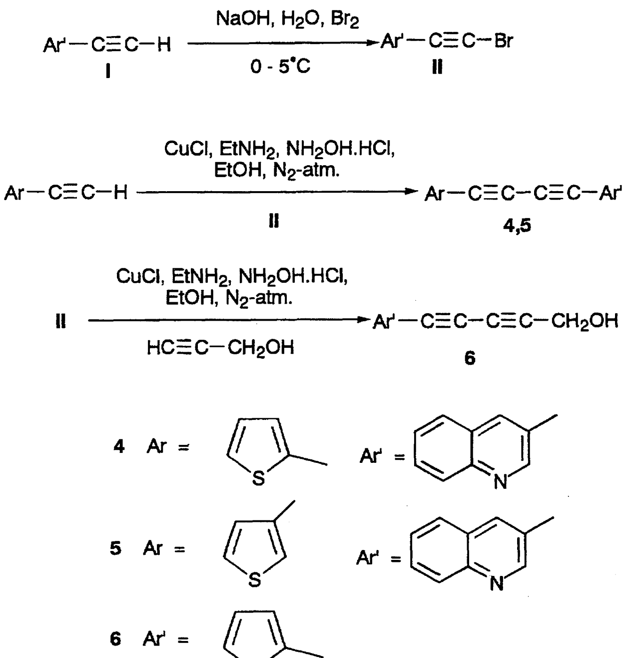
Preparation of the Monomers. The syntheses of 1,4-di-(2-thienyl)-1,3-butadiyne (**1**), 1,4-di(3-thienyl)-1,3-butadiyne (**2**), 1,4-di(3-benzo[*b*]thienyl)-1,3-butadiyne (**3**), 1-(3-quinolyl)-4-(2-thienyl)-1,3-butadiyne (**4**), 1-(3-quinolyl)-4-(3-thienyl)-1,3-butadiyne (**5**), and 5-(2-thienyl)-2,4-pentadiyne-1-ol (**6**) were carried out following routes shown in Schemes 1 and 2. The detailed procedures are being reported elsewhere.[17)]

Thermal Studies. Freshly crystallized and dried crystals were used for carrying out differential thermal analysis of the compounds. The samples were taken in aluminium pellets and sealed. They were kept in the cell of the calorimeter under nitrogen atmosphere. Differential scanning calorimetry measurements (DSCs) were run for different temperature ranges depending on the samples. Thermogravimetric analyses (TGA) were done using the same type of sealed aluminium pellets and heating the samples under nitrogen atmosphere from room temperature to adequately higher temperatures. TGA were recorded on Shimadzu DT-30 thermal analyzer. A Dupont 910 Differential Scanning Calorimeter equipped with a Thermal Analyst 2000 data processor was used to record DSCs.

Preparation of the Monomers. Hot stage micrographs were taken for the compounds at different temperatures under crossed polarizers. Freshly crystallized samples were taken on glass plates and were covered with cover-slips. The rate of heating was carefully controlled in order to observe the phase transitions properly. Optical microscopic observations were made using an Orthoplan Leitz microscope to which a Chaiz Meca heating-freezing stage (−190 °C to +600 °C) was attached.



Scheme 1. Synthetic route for symmetrical diynes.



Scheme 2. Synthetic route for unsymmetrical diynes.

Results and Discussion

The DSC of **1** showed an endotherm peak at 91.14 °C and an exotherm peak at 197.12 °C. It was observed that the end of endotherm transition and the beginning of exotherm were separated by a relatively large temperature region (Fig. 2). On the other hand, thermogravimetric analysis of compound **1** in the temperature region 30 to 300 °C, which is well beyond the exotherm region's limit, showed negligible weight loss.

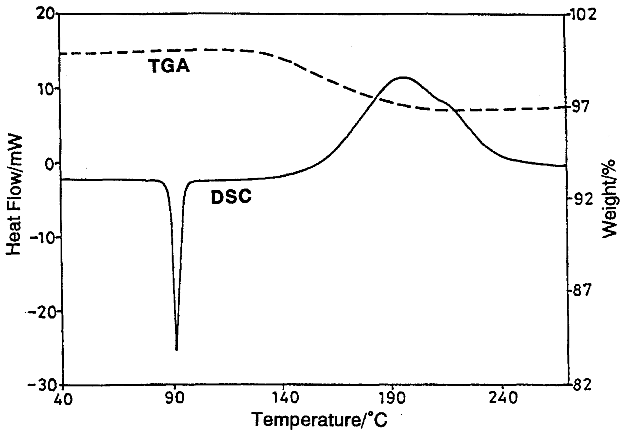


Fig. 2. Thermal analysis of 1: —— DSC, - - - TGA.

Monomer **2** also showed the same pattern upon DSC measurements. The endotherm peak was obtained at 109.97 °C, while the exotherm peak appeared at 232.38 °C. The temperature region between the end of endotherm transition and the beginning of exotherm was 42 °C. The thermogravimetric analysis showed only 3% weight loss in room temperature upon heating upto 300 °C. Similarly, DSC for samples **3**, **4**, **5**, and **6** exhibited endotherms and exotherms with temperature gaps of 30, 30, and 40 °C, respectively. Figures 3 and 4 show the DSC scans of **2**—**5**. Table 1 summarizes the results from the DSC measurements of all these diynes. In all these cases too, the weight loss was negligible as observed from their thermogravimetric analyses.

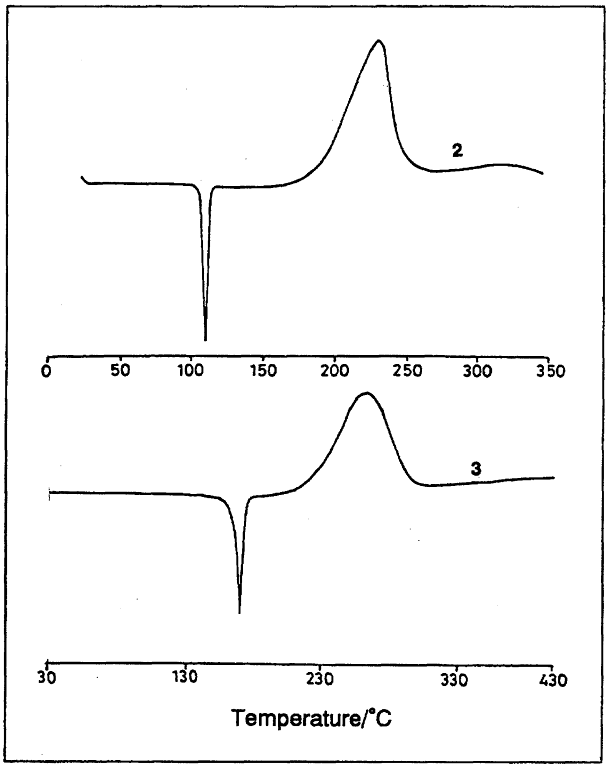


Fig. 3. Differential Scanning Calorimetry of diynes **2** and **3**.

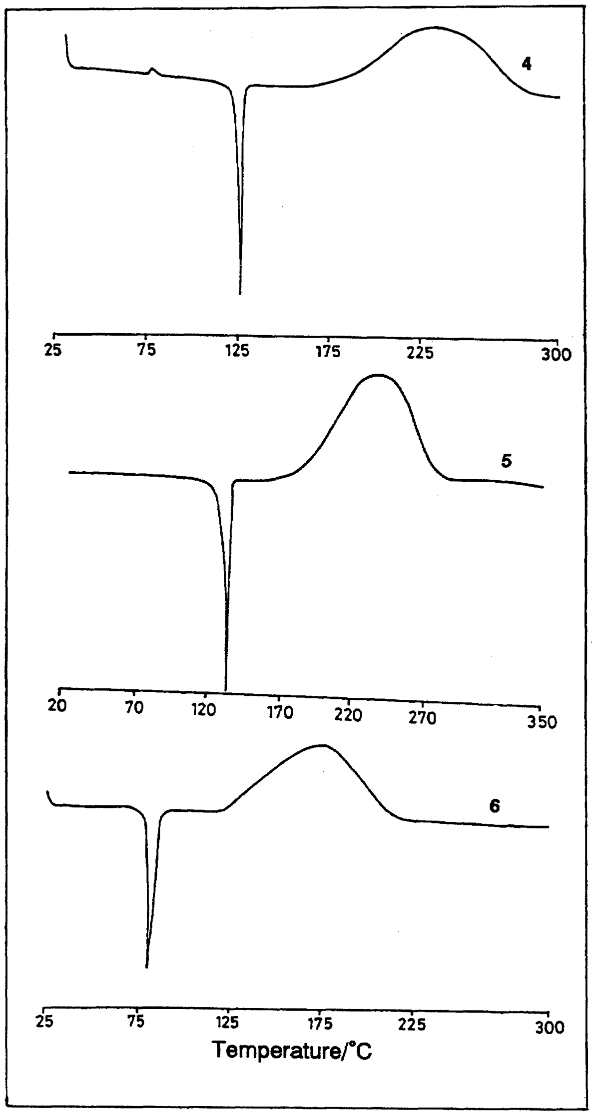


Fig. 4. Differential Scanning Calorimetry of diynes **4** to **6**.

DSC of diynes **1** to **6** indicated that they exhibit liquid crystalline behaviour upon annealing while no or negligible weight loss exhibited in their TGA suggested that they most probably have undergone polymerization reactions in liquid crystalline state. On the other hand, two other butadiynes, namely 1,4-di(3-quinolyl)-1,3-butadiyne (DQ) and 1,4-di(2-pyridyl)-1,3-butadiyne (DP) did not show any such behavior as observed from their DSC data.[18] In these cases, the endotherms are immediately followed by exotherms without any temperature gap. However, in these cases also, the thermogravimetric analysis showed negligible weight loss upon heating upto 300 °C suggesting that the exotherm peaks are due to a polymerization reaction.

The magnitudes of the endothermic phase transition are in the range 3.04 kcal mol^{-1}. This is less than the solid to liquid transition of 8.25 kcal mol^{-1} obtained by Barrall et al. for toluenesulphonate ester of 1,6-hexa-2,4-diyndiol and is of an order similar to the enthalpies obtained by Wu et al.,[20] Ozcayir and Blumstein,[21] and Milburn et al.[15] for the crystal to nematic phase change for 1,4-bis(alkylphenyl)-1,3-butadiynes. This observation substantiates the existence

Table 1. Enthapy Changes During Phase Transitions for the Diynes

Sample	Endotherm[a)] peak/(ΔH)[b)]	Exotherm[a)] peak/(ΔH)[b)]	Temperature (ΔT)[c)]	Color of product
1	91.14 (4.99)	197.12 (35.88)	100—135	Shining deep brown
2	110.27 (3.99)	232.38 (30.98)	120—162	Shining deep brown
3	170.81 (3.99)	261.83 (30.98)	180—210	Black
4	125.94 (4.13)	232.82 (26.93)	130—160	Black
5	133.06 (6.03)	234.21 (39.44)	140—240	Black
6	80.81 (3.99)	175.21 (30.98)	85—115	Black

a) Endotherm and Exotherm peaks are in °C. b) ΔH is in $\mathrm{kcal\,mol^{-1}}$. c) ΔT is the temperature gap (in °C) between the end of endotherm transition and beginning of exotherm.

Table 2. Cyclic DSC Results of the Diynes

Diyne	No. of cycle	ΔH of endotherm $\mathrm{kcal\,mol^{-1}}$	Endotherm °C
1	1	4.99	91.14
	2	4.56	90.85
	3	4.27	90.54
	4	4.05	90.21
2	1	3.99	110.27
	2	3.94	109.97
	3	3.56	109.86
	4	3.28	109.81
3	1	6.86	170.81
	2	6.62	170.58
	3	6.31	170.33
	4	6.06	170.14
4	1	4.13	125.94
	2	4.01	125.76
	3	3.82	125.51
	4	3.66	125.32
5	1	6.03	133.06
	2	5.81	132.81
	3	5.63	132.62
	4	5.49	132.38
6	1	3.04	80.51
	2	3.00	80.32
	3	2.91	80.22
	4	2.82	80.03

of liquid crystalline phases for the diynes **1** to **6** as discussed above.

Repeated cyclic DSC of all the diynes were done. While recording cyclic DSC, care was taken to heat the samples up to a temperature which is in the liquid crystalline region but not to heat the samples beyond the temperature where the exotherm begins. Thus, for **1**, heating was started at room temperature and stopped at 130 °C, which falls between the region of endotherm and exotherm. By selecting the temperature in this way, any possibility of irreversible chemical reaction was ruled out. Table 2 summarises the results of cyclic DSC done for the samples. It was observed that with each cycle the endotherm peak in DSC appears at a slightly lower temperature. Moreover, the ΔH for endotherm also goes on decreasing with increasing number of cycles. This suggests that the diynes undergo a certain reaction in the liquid crystalline region which should be a polymerization reaction as substantiated by TGA data. Due to conversion of monomer to polymer, the enthalpy change diminishes gradually and hence the decrease in area of the endotherm. On the other hand, polymer formation introduces a kind of impurity into the otherwise pure monomer which is manifested in the decrease of endotherm peak temperature.

The samples obtained after the DSC scans of **1**—**6** finished were taken out from the aluminium pellets. They had shining deep brown color. These products could not be dissolved in any common organic solvent nor in mineral acids. The elemental analysis of the compounds matched well with the elemental analysis of the corresponding monomers. Such results implied that the products formed are the polymers of the diynes. These products may be termed as melt polymers because they are formed in liquid crystalline phase.

To further probe the nature of the reaction, isothermal DSC was carried out for **1**. The sample was heated at 130 °C which falls in the range between endotherm and exotherm. After 6 h of annealing, the product was taken out of the DSC cell. The DSC scan did not show any significant shift from the baseline during the period of annealing. The product taken out after annealing was found to be a deep grey solid. The substance could be dissolved in dichloromethane. The thin layer chromatography (TLC) (petroleum ether : ethyl acetate/80 : 20) of this compound showed two spots. The spot having higher R_f value corresponded with that of **1**. Elemental analysis for the product from DSC cell matched well with that of the monomer **1** (Table 3). This suggests that the lower spot in TLC plate is due to the oligomer of **1** which may have formed during annealing in the DSC cell.

All the diynes were heated in a controlled manner on a hot stage while being observed through a microscope having a cross polarizer. The samples were heated up to the temperatures which immediately follow their respective endotherms. Thus, sample **1** became translucent upon reaching the endothermic temperature of 91.14 K. The nature of this translucent phase and subsequent reaction was examined under crossed polarizers of an optical microscope (Fig. 5). The translucent phase was identified as the nematic liquid crystalline phase. Upon shearing the sample, characteristic disclination structures were observed in the micrograph, they also showed birefringence when viewed under polarized light. Upon heating further, polymerization of the monomer occurred. The color of **1**, which was light yellow in the beginning of the liquid crystalline region, gradually darkened and became deep brown at the temperature corresponding

Table 3. Elemental Analysis Data of the Insoluble Parts Obtained from DSC Experiments of Diynes

Sample	Elemental analysis[a] (%)			
	C	H	N	S
1	66.96	2.78	—	29.22
	(67.25)	(2.82)		(29.57)
2	66.95	2.75	—	29.44
	(67.25)	(2.82)		(29.57)
3	76.35	3.18	—	20.22
	(76.40)	(3.20)		(20.40)
4	78.28	3.38	5.22	9.81
	(78.74)	(3.50)	(5.40)	(10.04)
5	78.54	3.42	5.21	9.92
	(78.74)	(3.50)	(5.40)	(10.04)
6	66.33	3.49	—	19.67
	(66.66)	(3.70)		(19.77)

a) Values in paranthesis are the calculated values for monomer.

Fig. 5. Photomicrograph of the nematic liquid crystal monomer of **1** at 98 °C between crossed polarizers (magnification: 1×50).

to DSC exotherm peak. Also, when the sample was heated isothermally at the temperature in the liquid crystalline region in hot stage microscope, the color of the monomer gradually darkened, although with a slower rate. The sample of **1**, polymerized at liquid crystalline phase, however, lost its liquid crystallinity. Similar results were observed for diynes **2** to **6**. All of them showed translucent phase at temperatures corresponding to the gap between endotherm and exotherm in their DSC. Thus, when compared with DQ and DP, for all the diynes above which contained sulfur atom in the heteroaromatic moiety, the crystal to nematic phase change was observed. Interestingly, no smectic phase was observed in any of the above mentioned diaynes. Previously also, researchers have reported such type of behavior in disubstituted diynes where only nematic phase was observed. However, this behavior is not a general one for diynes. For instance, Milburn et al. have reported diynes with phenyl side groups containing trifluoromethyl substitution where a smectic liquid crystalline phase was seen.[16] Thus, depending on the type of sidegroups in the diynes, one can expect a smectic phase as well along with a nematic phase.

Conclusion

We have investigated the thermal behaviour of diynes containing heteroaromatic moieties as directly bound sidegroups using differential scanning calorimetry, thermogravimetric analysis and by hot stage microscopy. Thermal parameters for the phase changes were obtained. For diynes with sulfur containing heteroaromatic sidegroups, a liquid crystalline phase was observed upon heating. The compounds undergo polymerization reactions in liquid crystalline phase but the polymerized samples were found to be opaque. All the samples showed nematic mesophase, while smectic phase was conspicuously absent. The substituent seems to play a role in deciding the thermal behavior, besides deciding the other properties of diynes. From our study on heteroaromatic functionalized diynes, sulfur seems to be the key to decide the thermal behavior.

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