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THE SYNTHESIS AND THERMAL PROPERTIES OF ISOMERIC ACETYLENE TERMINATED QUINOXALINES

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Nonmetallic Materials Division

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A mixture of the halogenated quinoxaline isomers, 3-(3-bromophenyl)-2-phenyl-6-iodoquinoxaline and 2-(3-bromophenyl)-3-phenyl-6-iodoquinoxaline, was synthesized and the two isomers were separated and purified. A substantial difference in solubility and melting point behavior was found between the isomers. The halogen terminated isomers were converted individually to the corresponding isomeric acetylene terminated quinoxalines which exhibited analogous solubility and melting point differences. The glass transition temperatures of the individual acetylene terminated quinoxalines and of various mixtures all fell within a

20. CONTINUED

range from 33°C to 54°C. The presence of isomer mixtures was found to inhibit reversion from the amorphous state to the crystalline state. The significance of this effect and of the solubility and melting point differences with respect to melt processing of acetylene terminated quinoxaline resin systems is discussed.

FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 2419, "Nonmetallic and Composite Materials," Task No. 241904, Work Unit Directive 24190415, "Structural Resins." It was administered under the direction of the Materials Laboratory, Air Force Wright Aeronatuical Laboratories, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold as the AFWAL/ML Work Unit Scientist. This report describes work conducted from January 1979 to June 1981.

The work described in this report was conducted by Dr. F. L. Hedberg, Marilyn R. Unroe, and Donna L. Bush. The manuscript was released by the authors in June 1983, for publication as a Technical Report.

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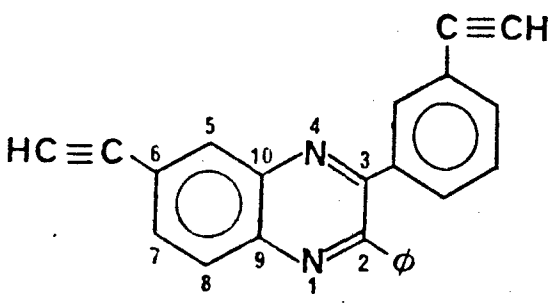
SECTION I

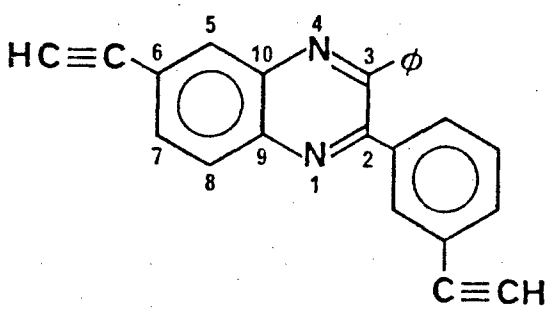
INTRODUCTION

The quinoxaline ring structure has been the basis of a variety of thermooxidatively stable, moisture resistant polymers for use in aerospace composites and adhesives. A recent development, in response to the need for melt processable resin systems, has been the preparation of thermosetting quinoxaline oligomers with terminal acetylene groups (References 1, 2, and 3). These acetylene terminated quinoxalines (ATQ's) exhibit low T_g values, a cure reaction through the acetylene groups at temperatures substantially above the softening temperature so that an adequate "window" for processing is obtained, and elevation of the T_g during the cure to the cure temperature used.

The fact that low initial T_g values are obtained for the ATQ's despite the presence of relatively rigid quinoxaline rings can be partially attributed to the mixture of oligomers in the case of oligomeric ATQ systems. A second factor is the presence of isomers which arise whenever different substituents are present at both the 2 or 3 position and the 6 or 7 position of the quinoxaline ring structure. The significant influence of isomer mixtures on the T_g of ATQ systems was seen in a recent study of small, monomeric ATQ systems with no oligomers or flexibilizing phenyl ether linkages (Reference 4). It was found that the isomeric mixture of 6-ethynyl-3-(3-ethynylphenyl)-2-phenylquinoxaline (Ia) and 6-ethynyl-2-(3-ethynylphenyl)-3-phenylquinoxaline (Ib) showed a T_g of 20°C.



Ia



Ib

A recent Russian paper has shown that ^{13}C NMR can be used as a tool to distinguish between quinoxaline isomer sites in polyphenylquinoxalines (Reference 5). In the same paper, it was also shown that the isomer ratio could be varied over approximately a 20% range in model compounds by the appropriate choice of synthesis solvent. In a high molecular weight polymer, such a range would probably have little effect on physical properties. In the case of small quinoxaline molecules such as some ATQ systems, however, such a range could have a significant effect on the T_g and associated processability, if the individual isomers have significantly different T_g values or viscosity-temperature values.

One possible role of the isomer mixture in affording a low T_g value for such ATQ systems might be by inhibiting the formation of crystallinity, thereby locking in the amorphous state. Since there are no reports in the literature of the isolation and properties of individual quinoxaline isomers, the possibility cannot be ruled out either that one isomer might have an anomalously high T_g value, or that crystallinity might not be easily achieved or maintained for the pure isomers and both isomers possessed low T_g values. To obtain a low T_g material in the former case would require either an isomer mixture or a stereospecific synthesis of the isomer with the lower T_g value. In the latter case, variable compositions of isomers could be used to afford adequate melt processability.

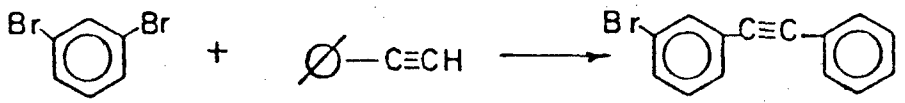
In this paper, we report the preparation of the quinoxaline isomer mixture of 3-(3-bromophenyl)-2-phenyl-6-iodoquinoxaline (IIa) and 2-(3-bromophenyl)-3-phenyl-6-iodoquinoxaline (IIb), and the isolation of the individual isomers IIa and IIb together with their conversion to the isomers Ia and Ib. The unique physical and thermal properties of these isomers is discussed, as well as the implication of these findings with respect to the synthesis and utilization of ATQ resin systems.

SECTION II

RESULTS AND DISCUSSION

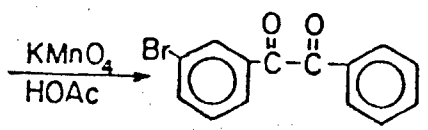
A. SYNTHESIS

3-Bromobenzil IV was synthesized in an overall 68 per cent yield according to the reaction sequence shown below (Equation 1):



III

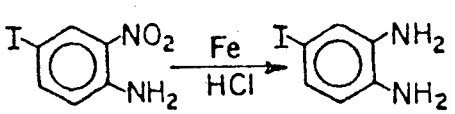
(1)



IV

3-Bromodiphenylacetylene (III) was produced in 73 per cent yield by the palladium catalyzed phenylethynylation (Reference 6) of m-dibromobenzene. Oxidation of 3-bromodiphenylacetylene to 3-bromobenzil (IV) in 93 per cent yield was effected by a modification of the method of Lee and Chang (Reference 7) with potassium permanganate in acetone. The yield of IV obtained from 1, 3-dibromobenzene without isolating and purifying III was 48.5 per cent.

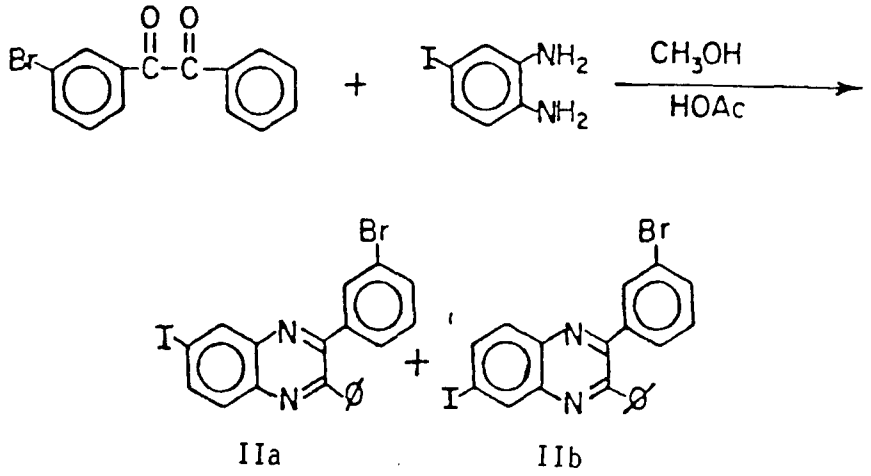
2-Amino-4-iodoaniline (V) was prepared in 82 per cent yield by reducing 4-iodo-2-nitroaniline (Reference 8) using iron powder in concentrated hydrochloric acid (Equation 2) according to a reported procedure (Reference 9).



V

(2)

The condensation of equimolar quantities of 3-bromobenzil and 4-iodo-o-phenylenediamine afforded a mixture of 3-(3-bromophenyl)-2-phenyl-6-iodoquinoxaline (IIa) and 2-(3-bromophenyl)-3-phenyl-6-iodoquinoxaline (IIb) as shown in Equation 3. Analysis of the



IIa IIb (3)

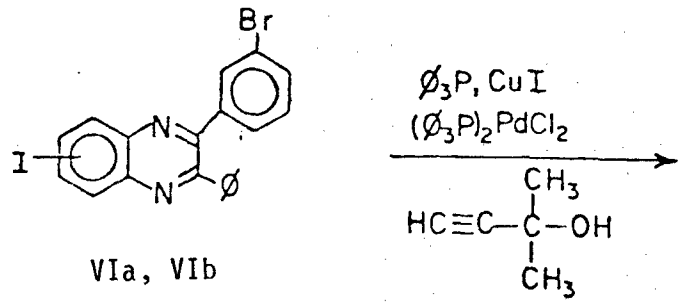
reaction mixture by TLC indicated the formation of two products of slightly different R_f values. Fractional recrystallization of the reaction residue afforded the product of lower R_f value in pure form. Purification of the higher R_f product was much more difficult, requiring careful column chromatography of the mother liquor residue followed by recrystallization to afford pure material. Purity was determined both by TLC analysis and, more precisely, by the ^{13}C NMR spectra of the two isomeric products. In the latter analysis, the C-2 and C-3 positions were found to be distinct for each product.

The low R_f isomer, mp. 182°-184°C, was assigned the structure IIa, based upon both x-ray crystallographic evidence and a ^{13}C NMR study carried out on a sample of low R_f isomer synthetically enriched with ^{13}C at the C-2 position. Details of the x-ray and ^{13}C NMR studies will be reported at a later date (Reference 10).

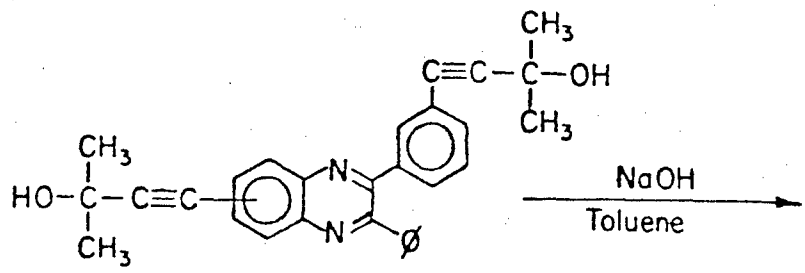
The high R_f product, mp. 95°C, was determined by elemental composition, molecular weight, proton NMR spectrum and infrared spectrum to be isomeric with Ia, and was thus assigned the structure IIb.

6-Ethynyl-3-(3-ethynylphenyl)-2-phenylquinoxaline (Ia) and 6-ethynyl-2-(3-ethynylphenyl)-3-phenylquinoxaline (Ib) were prepared from isomers IIa and IIb respectively, by the palladium catalyzed substitution of the halogens with

2-methyl-3-butyn-2-ol to afford the acetone adducts 6-(2-hydroxy-2-methylbut-3-ynyl)-3-[3-(2-hydroxy-2-methylbut-3-ynyl)phenyl]-2-phenylquinoxaline (VIa) and 6-(2-hydroxy-2-methylbut-3-ynyl)-2-[3-(2-hydroxy-2-methylbut-3-ynyl)phenyl]-3-phenylquinoxaline (VIb) followed by basic cleavage of acetone to free the ethynyl groups (Equation 4).

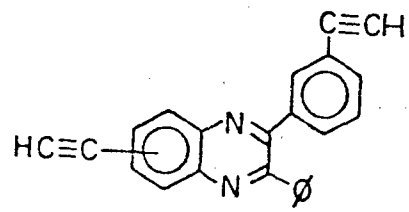


VIa, VIb



VIa, VIb

(4)



Ia, Ib

Compounds VIa and VIb were isolated in 50 and 70 per cent yields respectively and were purified by recrystallization from cyclohexane. The diethynyl compounds Ia and Ib were obtained from VIa and VIb in 55 and 91 per cent yields respectively.

Compound Ia was recrystallized from methanol while compound Ib was purified by column chromatography, since good crystallization could not be achieved from any solvents with this compound.

A striking difference between the members of each set of isomers Ia-Ib and IIa-IIb which became apparent during the synthesis was the low solubility of both isomer Ia and its precursor IIa in alcoholic solvents, relative to their isomeric counterparts Ib and IIb. It was this significant solubility difference which permitted the separation of IIa from IIb. Alcoholic solvents are standardly used to purify higher molecular weight acetylene terminated quinoxalines with which precipitation is virtually quantitative. For lower weight acetylene terminated quinoxalines such as the mixture of 3,3'-bis(4-[3-ethynylphenoxy]phenyl)-2,2'-diphenyl-6,6'-biquinoxaline with its 2,2'-3,3' and 2,3'-2',3 isomers (Reference 1), however, a substantial solubility difference among the isomers could result in isomer distributions which are dependent upon the work-up conditions used. A secondary effect could be the formation of crystalline domains of high concentrations of individual isomers. The impact of such effects on the processing of acetylene terminated quinoxalines is discussed subsequently under thermal characterization and conclusions.

B. THERMAL CHARACTERIZATION

Thermal characterizations on compounds Ia, Ib, IIa, IIb; 1:1, 3:1, and 1:3 mixtures of Ia and Ib; and a 1:1 mixture of IIa and IIb were carried out by differential scanning calorimetry (DSC). The initial DSC scans showed endotherms corresponding to crystalline melting points ($T_{m's}$). These scans were stopped just after the highest T_m value and the samples were cooled rapidly to -50°C. Subsequent scans revealed endothermic transitions typical of glass transition temperatures ($T_{g's}$). In the case of compounds Ia, Ib, and their mixtures, an exothermic transition corresponding to the thermal cure reaction of terminal acetylene groups also appeared. The data obtained is summarized in Table 1, and the composites of scans for each sample are shown in Figures 1 thru 8.

In the case of the analogously structured, higher melting isomer in each pair, Ia and IIa, two T_m values were obtained, with the lower value appearing during a second scan and preceeded by an exotherm corresponding to crystallization from the amorphous state (Figures 1 and 3). X-ray crystallographic analysis of IIa (Reference 10)

TABLE 1

THERMAL TRANSITIONS OF QUINOXALINE ISOMERS AND ISOMER MIXTURES

Sample	T_m(°C)	T_g(°C)	T_{max}(°C)
IIa	182,165*	38	----
IIb	94	41	----
Ia	182,169*	54	240
Ib	121	33	218
1:1 IIa & IIb	95,125	38(40)**	----
1:1 Ia & Ib	79,109	34(41)**	240
3:1 Ia & Ib	105,170	42(47)**	217
1:3 Ia & Ib	138	33(37)**	219

*Obtained on second cycle.

**Theoretical T_g calculated by the method of Fox and Loshek (Reference 11).

confirmed the presence of two distinct isomorphic crystalline structures. The higher melting isomorph of IIa (and presumably of Ia) is apparently favored upon crystallization from solution, while the lower melting isomorphic form is the favored structure when crystallization occurs from the molten amorphous state. The isomorphic T_m values were significantly higher for both Ia and IIa than the single T_m value obtained for their isomeric counterparts Ib and IIb.

Two broad T_m endotherms appeared in three of the four mixtures of isomers (Figures 5, 6 and 8). This phenomenon is most likely due to separation of distinct microcrystalline domains during removal of solvent from the mixtures. The one mixture in which a single T_m endotherm occurred (Figure 7), corresponding to a true eutectic, is the mixture of Ia and Ib in which the main constituent is the lower melting and more soluble isomer Ib. The naturally formed mixture of Ia and Ib had been previously reported (Reference 4) to show a single T_m endotherm at 129°C, as compared with the T_m values of 29°C and 109°C shown in Table 1 for the 1:1 mixture. Any comparison between the naturally formed mixture and the prepared mixture, however, is rendered very difficult because the actual amounts of Ia and Ib are not known for the natural mixture, different solvents were removed (chloroform for the natural mixture and methylene chloride for the 1:1 mixture), and the DSC heating rates were different (20°C/minute for the natural mixture and 10°C/minute for the 1:1 mixture).

The T_g values obtained for the sets of pure isomers showed considerably smaller differentials. In the case of Ia and Ib, the higher melting isomer, Ia, showed the higher T_g value of 54°C versus 33°C for Ib. The opposite situation occurred with IIa and IIb for which the lower melting isomer, IIb, showed the higher T_g value of 41°C versus 38°C for IIa. The amorphous states obtained with both Ia and IIa were not very stable as evidenced during continuation of the second DSC scan past the T_g. At 100°C and at 116°C for Ia and IIa, respectively, exothermic transitions corresponding to crystallization occurred. These exotherms were subsequently followed by T_m endotherms at 165°C for Ia and at 169°C for IIa, corresponding to the lower melting isomorphic form of each of these compounds.

For ease of processing acetylene terminated resins such as Ia and Ib, a broad window is desirable between the T_g and the onset of cure. Both isomers Ia and Ib

possess low enough T_g values to provide an adequate window for processing. The natural mixture of Ia and Ib obtained from the non-stereoselective synthesis thus provided no significant advantage in T_g value over that obtained from the individual isomers. The true advantage of the isomer mixture appears to be the inhibiting effect of the mixture upon the tendency of the individual isomers to crystallize, thus locking in the low T_g amorphous state.

SECTION III

CONCLUSIONS

The significant solubility differences shown by the acetylene terminated isomers Ia and Ib should be taken into account during the purification of any ATQ resin systems of relatively small size. In addition to the obvious effect upon yield caused by selective removal of the more soluble isomer, the effects upon processing caused by selective enrichment in the less soluble isomer should be considered. Thermodynamic considerations are in agreement with the fact that the less soluble isomer should exhibit the higher crystalline melting point, as was the case with Ia. Enrichment of an ATQ mixture in the higher melting isomer will raise the initial temperature required to remove all of the crystallinity to a point where some premature curing could occur, as can be seen from the T_m values for the Ia-Ib mixtures in Table 1, and will also enhance the tendency of the mixture to revert from the amorphous back to the crystalline state, thereby lessening the time permitted for adequate processing.

SECTION IV

EXPERIMENTAL

General

Unless otherwise noted chemicals and solvents were obtained from commercial suppliers and were used without further purification. The following is a list of chemicals used in the syntheses and their sources:

1. M-Dibromobenzene (Aldrich Chemical Co., reagent)

2. Phenylacetylene (Farchan Division, CHEMSAMPCO, Inc., reagent)

3. Cuprous iodide (CuI) (Alfa Products, 98%)

4. Triphenylphosphine ($(C_6H_5)_3P$) (Aldrich Chemicals, 99%)

5. Dichlorobistriphenylphosphine palladium ($((C_6H_5)_3P)_2PdCl_2$) (Strem Chemicals, Inc., reagent)

6. o-Nitroaniline (Matheson, Coleman, and Bell, reagent)

7. 2-Methyl-3-butyn-2-ol (Aldrich Chemical Co., reagent)

Unless otherwise stated, the following procedures were used in the syntheses. Solvents were removed by evaporation under reduced pressure using a Buchi/Brinkman Rotavapor R apparatus. All reactions were conducted in a nitrogen atmosphere and monitored by thin layer chromatography (TLC) using Bakerflex silica gel strips IBF. Melting points were determined with a Fisher 355 digital melting point analyzer or a Mel-temp melting apparatus and are uncorrected. Infrared (IR) spectra were determined with a Beckman IR-33 spectrophotometer. ^{1}HNMR spectra were determined using one of the following spectrometers: Varian EM-360A or a Varian XL-100 (15). The spectra were recorded at 60 and 100 MHz respectively. Chemical shifts were expressed in parts per million (ppm) downfield from internal tetramethylsilane (TMS). ^{13}CNMR spectra were determined on a Varian XL-100 (15) spectrometer equipped

with a Varian VFT-100 computer accessory and Gyrocode decoupler by the polymer group at the Air Force Wright Aeronautical Materials Laboratory, Wright-Patterson AFB, Ohio. The spectra were recorded at 25.2 MHz using spectral widths of 5 or 2.5 KHz. Chemical shifts were measured from $CDCl_3$ and converted to the TMS scale using $CDCl_3$-TMS = 76.91 ppm. Mass spectra and elemental analyses were performed by the analytical group at the Air Force Wright Aeronautical Materials Laboratory, Wright-Patterson AFB, Ohio. Mass spectra were obtained using a DuPont 21-490 spectrometer modified for chemical ionization and equipped with a DuPont mass marker. A Hewlett-Packard 5700 A gas chromatograph with a silicone interface was used in conjunction with the mass spectrometer. Mass spectra data were obtained as oscillographic recordings on light sensitive paper and reported as m/e (mass per unit charge). Microanalyses were determined using a Perkin-Elmer 240 C, H, and N analyzer. The elemental analyses of halogens were determined using the Schoniger combustion technique. Oxygen analyses were determined by either the Unperzaucher technique or by using a modified Perkin-Elmer 240 analyzer. Differential scanning calorimetry (DSC) values for T_g, T_m, and T_{max} for cure exotherm were determined, using one of the following calorimeters: a DuPont 900 at 10°C per minute with an argon flow or a Perkin-Elmer DSC-2 at 10°C per minute with a nitrogen flow. Two scans were recorded for each sample; the first was a complete scan from -50°C to 400°C. In the second, the sample was heated until the T_m was recorded, the calorimeter was turned off, the samples cooled at -50°C (liquid nitrogen), and finally reheated to 400°C to record the T_g and T_{max}.

Isomeric mixtures were prepared by mixing calculated quantities of the isomers in CH_2Cl_2, evaporating the solvent, and drying the samples at 54°C and 3.5 mm Hg for 2 h. Column chromatography was performed with Woelm Pharma silica gel (activity III/30 mm) containing 0.5% inorganic fluorescent indicator for short-wave UV (254 nm).

Synthesis of 3-Bromobenzil (IV)

3-Bromodiphenylacetylene was prepared from the reaction of equimolar amounts of phenylacetylene and m-dibromobenzene using the palladium catalysis technique of Sabourin (Reference 6). Phenylacetylene (12.91 g, 126.57 mmol) in 100 mL $(CH_3CH_2)_3N$ was added dropwise with rapid stirring to a mixture of m-dibromobenzene (30 g, 127.2 mmol), 0.8 g $(C_6H_5)_3P$, 0.2 g CuI, and 0.2 g $((C_6H_5)_3P)_2PdCl_2$ in 700 mL

$(CH_3CH_2)_3$ N. The reaction mixture was gently refluxed for 2 h. The reaction progress was monitored by TLC with petroleum ether as the developing solvent. The reaction mixture was poured into a solution of 510 mL concd H_2SO_4 and 1 Kg of ice, stirred 20 min, extracted three times with 200 mL CH_2Cl_2, washed two times with 450 mL water, and concentrated to dryness. The crude product mixture of 3-bromodiphenylacetylene, 1,3-bis(phenylethynyl)benzene and unreacted m-dibromobenzene was oxidized with $KMnO_4$ by a reported procedure for benzil synthesis (Reference 7). Adogen 464 (methyl-trialkyl(C_8C_{10})-ammonium chloride) (19.3 g) and 30 mL glacial acetic acid were added to 29.3 g of crude material dissolved in 200 mL CH_2Cl_2. After stirring the organic mixture 15 min, a solution of $KMmO_4$ (prepared from 59.25 g in 1125 mL water) was added and the mixture was refluxed 2 h. TLC(CCl_4) indicated that the crude product contained two major compounds: 3-bromobenzil and 1,3-bis(phenylglyoxaloyl)benzene. After cooling the reaction solution for 40 min, reaction of the excess $KMnO_4$ was effected by the addition of 20.4 g $NaHSO_3$ over a 10 min interval, followed by the portionwise addition of 96 mL concd HCl. After stirring the reaction solution for 10 min, an additional 35.25 g $NaHSO_3$ was added over a 10 min interval. The light yellow organic layer was separated from the water layer, washed two times with 450 mL water, and concentrated to dryness. The residue was dissolved in 50 mL CCl_4, stirred with $MgSO_4$ (10 g), filtered, and chromatographed through a quartz column of silica gel using CCl_4 as the elutant. Two products were obtained: 1,3-bis(phenylglyoxaloyl)benzene (4.67 g) and 3-bromobenxil. Fractions containing the latter were combined in 100 mL of CH_2Cl_2:heptane(1:2), heated, crystallized, filtered, and dried at 60°C and 3.5 mm Hg to yield 15.83 g (48.5%), mp 80-81°C. IR(neat) 3070 cm^{-1} (Ar-H), 1660 cm^{-1} (C=O); ^{1}HNMR($CDCl_3$) δ 7.65 (m, Ar-H); Anal. Calcd. for $C_{14}H_9BrO_2$: C, 58.13; H, 3.11; Br, 27.65. Found: C, 58.26: H, 2.78: Br, 27.33: MS calcd for $C_{14}H_9BrO_2$: M^+, 289,291; Found: M^+, 289, 291.

Purification of 3-Bromodiphenylacetylene (III)

The crude product mixture of 3-bromodiphenylacetylene and 1,3-bis(phenylethynyl)benzene was purified by column chromatography. The mixture was dissolved in 50 mL CCl_4, stirred over 10 g $MgSO_4$, filtered and chromatographed through a quartz column of silica gel (598 g) using CCl_4 as the elutant. The fractions containing the desired product were identified by TLC (petroleum ether), combined, evaporated to dryness and dissolved in 120 mL of CH_3OH:$CHCl_3$(3:1), concentrated to 75ml, cooled (acetone-dry ice, and the resulting crystals filtered to yield

3-bromodiphenylacetylene (11.91 g, 73%, mp 32-33°C; IR (neat) 2215 cm^{-1} (C≡C); ^{1}HNMR ($CDCl_3$) δ 7.47 (m, Ar-H): Anal. Calcd for $C_{14}H_9Br$: C, 65.37: H, 3.50: Br, 31.3. Found: C, 65.43; H, 3.29; Br, 30.73: MS calculated for $C_{14}H_9Br$: M^+; 256-258; Found: M^+; 256-258.

The Oxidation of III to IV

To a solution of 3-bromodiphenylacetylene (6 g, 23.3 mmol) in 400 mL acetone and 102 mL glacial acetic acid was added 18.4 g $KMnO_4$. After stirring the resulting mixture for 3 h at room temperature, it was added to a solution of 91.7 g $NaHSO_3$ in 910 mL water, stirred 5 min, and extracted four times with 200 mL CH_2Cl_2. The combined CH_2Cl_2 extracts were washed two times with 400 mL of water, concentrated to dryness, and chromatographed on silica gel using CCl_4 as the elutant. The fractions containing the desired product were evaporated to dryness, dissolved in 125 mL of heptane: CH_2Cl_2 (4:1), concentrated to 60 mL, and cooled for 8 h. The resulting crystals were filtered, washed with cold heptane, and dried at 54°C and 3.5 mm Hg to yield 6.26 g of 3-bromobenzil (93%), mp 79-80°C.

Synthesis of 4-Iodo-2-nitroaniline

4-Iodo-2-nitroaniline was prepared by treatment of 2-nitroaniline with ICl according to the procedure of M. P. Brenans (Reference 8). 2-Nitroaniline (125 g, 904.9 mmol) in 750 mL glacial acetic acid was added to a solution of ICl (172.5g, 1062.45 mmol) in 350 mL glacial acetic acid. The mixture was stirred 2 h at 23°C and poured into water. The resulting precipitate was filtered, washed with water, and recrystallized from ethanol (5 mL/g) to yield 212.3 g (89%) 4-iodo-2-nitroaniline mp 121-123°C, [(lit. (Reference 8) mp 122°C)]; IR(KBr)-3385 cm^{-1} (NH_2), 1540 cm^{-1},1325 cm^{-1} (NO_2), 800 cm^{-1} (N-H wag); ^{1}HNMR($CDCl_3$) δ 6.19 (br-s, 2H,NH_2), 6.68 (d,1H,H-6), 7.7 (d of d, 1H, H-5), 8.6 (d, 1H, H-3).

Synthesis of 2-Amino-4-iodoaniline (V)

This compound was synthesized by a modification of the reduction technique reported by Feitelson et al. (Reference 9). Iron powder (175.4 g, 3140 mmol) was added portionwise over a 35 minute interval to a suspension of 4-iodo-2-nitroaniline (80 g, 303 mmol) in 1196 mL concd HCl. After stirring the reaction mixture at

ambient temperature for 4 h, the resulting precipitate was collected by suction filtration, washed with 500 mL HCl, and dried overnight under reduced pressure. The precipitate was stirred in 1050 mL hot saturated $NaHCO_3$ and filtered after 20 min. The filtrate was extracted with 200 mL CH_2Cl_2. The crude product was dissolved in 800 mL CH_2Cl_2 and filtered through celite. The CH_2Cl_2 solutions were combined and evaporated to dryness. The product was decolorized with 3 g activated charcoal and recrystallized from 3:1 hexane: CH_2Cl_2 to yield 2-amino-4-iodoaniline (58.15 g, 82%), mp 74-76°C, (lit. (Reference 9) mp 73°C); IR (KBr 3420 cm^{-1}, 3350 cm^{-1}, 3290 cm^{-1} (NH_2), ^{1}HNMR ($CDCl_3$) δ 7.0 (m, 2H, Ar-H), 6.48 (d, 1H, Ar-H), 3.35 (s, 4H, NH_2).

Synthesis and Separation of 3-(3-Bromophenyl)-2-phenyl-6-iodoquinoxaline, (IIa), and and 2-(3-Bromophenyl)-3-phenyl-6-iodoquinoxaline (IIb)

3-Bromobenzil (37.05 g, 128.2 mmol), 4-iodo-o-phenylenediamine (30 g, 128.2 mmol), and 500 mL CH_3OH were combined in a reaction vessel and stirred 15 min before the addition of 10 mL glacial acetic acid. The reaction mixture was refluxed for 2 h and stirred an additional 20 h at ambient temperature.

The reaction progress was monitored by TLC (8:1 petroleum ether: ether). The reaction mixture was evaporated to dryness and dried at 25°C and 3.5 mm Hg for 24 h to yield 62.17 g (99.6%) of the isomer mixture. Separation of the isomers was achieved by the following procedure. A 20 g (41.07 mmol) portion of the isomer mixture was dissolved in 600 mL of CH_3OH:CCl_4(2:1), concentrated to 200 mL, left to crystallize for 18 h, and filtered. After four additional recrystallizations in C_2H_5OH:$CHCl_3$(2:1) the pure isomer was obtained (6.6 g, 32.8%), mp 182-184°C. The IR and ^{1}HNMR data obtained were consistent with the proposed aromatic structure; ^{13}CNMR ($CDCl_3$) see Table II; Anal. Calcd for $C_{20}H_{12}BrIN_2$: C, 49.31; H, 2.49; Br, 16.4; I, 26.1; N, 5.75. Found: C, 49.32; H, 2.23; Br, 16.30; I, 25.70; N, 5.51; MS Calcd for $C_{20}H_{12}BrIN_2$: M^+, 486,488; Found: M^+ 486,488.

Column chromatography afforded the best yield of the 3-(3-bromophenyl)isomer. The crude mixture (1 g) was dissolved in 10 mL hot $CHCl_3$, combined with 100 mL hot CH_3CH, left to cool 18 h at ambient temperature, and filtered. The filtrate was evaporated to dryness and subsequently purified using column chromatography. The crude isomer (0.44 g) was eluted with CCl_4 followed by CCl_4: toluene (4:1) on a

359 g silica gel column. Fractions 1-3, which contained the desired product, were combined in 50 mL hot CH_3OH, cooled at -5°C for 7 days, filtered, washed with 10 mL cold CH_3OH, dried at 54°C and 3.5 mm Hg to yield 0.29 g (28.7%) mp 95°C. The IR and ^{1}HNMR data obtained were consistent with the expected aromatic structure; ^{13}CNMR ($CDCl_3$) see Table II; MS Calcd for $C_{20}H_{12}BrIN_2$: M^+, 486,488. Found: M^+, 486,488. Anal. Calcd for $C_{20}H_{12}BrIN_2$: C, 49.3; H, 2.49; Br, 16.4; I, 26.1; N, 5.75. Found: C, 49.43; H, 2.25; Br, 16.22; I, 25.03; N, 5.71.

Synthesis of 6-(2-Hydroxy-2-methylbut-3-ynyl)-3-[3-(2-hydroxy-2-methylbut-3-ynyl)phenyl]-2-phenylquinoxaline (VIa)

2-Methyl-3-butyn-2-ol (2.6 g, 30.9 mmol) was added dropwise with rapid stirring to a mixture of 2-(3-bromophenyl)-3-phenyl-6-iodoquinoxaline (5 g, 10.3 mmol), 0.8 g $(C_6H_5)_3P$, 0.2 g CuI, and 0.2 g $((C_6H_5)_3P)_2PdCl_2$ in 200 mL $(C_2H_5)_3N$ at 90°C. The reaction was refluxed 20 h, concentrated to dryness, dissolved in 200 mL CH_2Cl_2, poured into an acid solution (prepared from 100 mL concd H_2SO_4 in 500 g ice), and stirred 20 min. The organic layer was separated, washed two times with 450 mL water, and concentrated to dryness. The crude product was dissolved in 50 mL CH_2Cl_2, stirred with 15 g $MgSO_4$, filtered, and chromatographed on a quartz column using silica gel. The column was eluted with 600 mL of CH_2Cl_2: ether (6:1) followed by 1250 mL of CH_2Cl_2: ether (4:1), 600 mL CH_2Cl_2: ether (6:1), 600 mL CH_2Cl_2: ether (4:1), and finally by 600 mL of CH_2Cl: ether (2:1), and six fractions were collected. Fractions 3-6, which contained the desired product, were concentrated, combined, added to 250 mL of cyclohexane: CH_2Cl_2 (4:1), and concentrated to 200 mL. The yellow crystals were filtered, washed two times in 10 mL cold cyclohexane, and dried at 62°C and 3.5 mm Hg for 3.5 h to yield 2.42 g (50%) mp 152.4-154.5°C, IR (KBr) 3300-3400 cm^{-1}(O-H), 3070 cm^{-1} (Ar-H), 2995 cm^{-1}, 2940 cm^{-1} (-CH_3), 2230 cm^{-1} (C≡C), 1160 cm^{-1} (C-OH); ^{1}HNMR ($CDCl_3$) δ 7.79 (m, 12H, Ar-H), 2.3 (s, 2H, O-H), 1.67 (s, 6H, C-H_3), 1.57 (s, 6H, C-H_3). MS Calcd for $C_{30}H_{26}N_2O_2$: M^+, 446. Found: M^+, 446. Anal. Calcd for $C_{30}H_{26}N_2O_2$: C, 80.72; H, 5.83; N, 6.28; O, 7.17. Found: C, 80.71; H, 5.85; N, 6.00; O, 7.95.

Synthesis of 6-(2-Hydroxy-2-methylbut-3-ynyl)-2-[3-(2-hydroxy-2-methylbut-3-ynyl)phenyl]-3-phenylquinoxaline (VIb)

2-Methyl-3-butyn-2-ol (0.54 g, 6.42 mmol) was added dropwise with rapid stirring to a mixture of 3-(3-bromophenyl)-2-phenyl-6-iodoquinoxaline (0.7 g, 1.44 mmol), 0.2 g $(C_6H_5)_3P$, 0.05 g CuI, and 0.05g $((C_6H_5)_3P)_2PdCl_2$ in 60 mL $(CH_3CH_2)_3N$ at 90°C. The reaction solution was refluxed for 24 h.

The reaction solution was evaporated to dryness, dissolved in 200 mL CH_2Cl_2, combined with an acid solution (prepared from 75 mL concd H_2SO_4 in 500 g ice), and stirred 20 min. The CH_2Cl_2 layer was separated from the aqueous layer, washed two times with 200 mL water, concentrated to 50 mL, stirred with 10 g $MgSO_4$, and filtered. The solution was chromatographed through a quartz column of 400 g of Fisher (100-200 mesh) florasil. The column was eluted with 500 mL CH_2Cl_2, followed by 6550 mL of CH_2Cl_2:ether (6:1), and finally 1400 mL of CH_2Cl_2:ether (6:2) and six fractions were collected. Fractions 3-6 were combined, concentrated to 25 mL, and added to 50 mL cyclohexane. The solution was concentrated to 50 mL to promote crystallization. The yellow solid was filtered, washed in cold cyclohexane and dried at 60°C and 3.5 mm Hg for 2 h to yield 0.51 g (79%) mp 85.5-86.2°C; IR (KBr) 3440-3300 cm^{-1} (O-H), 3070 cm^{-1} (Ar-H), 2995 cm^{-1}, 2940 cm^{-1}($-CH_3$), 2230 cm^{-1}(C≡C), 1165 cm^{-1} (C-OH); ^{1}HNMR($CDCl_3$) δ 7.76 (m, 12H, Ar-H), 2.56 (br s, 1H, O-H), 2.38 (br s, 1H, O-H), 1.65 (s, 6H, C-H_3). 1.6 (s, 6H, C-H_3). MS Calcd for $C_{30}H_{26}N_2O_2$: M^+, 446. Found: M^+, 446; Anal. Calcd for $C_{30}H_{26}N_2O_2$: C, 80.72; H, 5.83; N, 6.28; O, 7.17. Found: C, 80.48; H, 5.73; N, 6.43; O. 7.25.

Synthesis of 6-Ethynyl-3-(3-ethynylphenyl)-2-phenylquinoxaline (Ia)

A solution of 1 g NaOH in 20 mL CH_3OH was added with caution to a warmed solution of 6-(2-hydroxy-2-methylbut-3-ynyl)-3-(2-hydroxy-2-methylbut-3-ynylphenyl)-2-phenylquinoxaline (2.35 g, 5.27 mmol) in 600 mL toluene in a reaction vessel fitted with a distillation apparatus. The reaction mixture was distilled until 500 mL of distillate was collected and the remaining solution was evaporated to dryness. The residue was dissolved in 50 mL CH_2Cl_2, stirred with 8 g $MgSO_4$, filtered, and poured onto a quartz column containing silica gel. The product was eluted with CH_2Cl_2 and stripped of solvent. The residue was dissolved in 200 mL of benzene: heptane (1:1), decolorized with 0.5 g charcoal, filtered, and added to a flask

containing 20 mL hot CH_3OH. After standing overnight the product was separated by filtration, washed two times with 10 mL cold CH_3OH, and dried at 65°C and 3.5 mm Hg for 2 h to yield 0.96 g (55%) mp 182°C; IR (neat) 3310 cm^{-1} (C≡C); ^{1}HNMR ($CDCl_3$) δ 7.73 (m, 12H, Ar-H), 3.28 (s, 1H, ≡C-H), 3.05 (s, 1H, ≡C-H), ^{13}CNMR, see Table 2, MS Calcd for $C_{24}H_{14}N_2$: M^+, 330. Found: M^+, 330. Anal. Calcd: C, 87.27; H, 4.24; N, 8.24. Found: C, 87.58; H, 3.77; N, 8.29.

Synthesis of 6-Ethynyl-2-(3-ethynylphenyl)-3-phenylquinoxaline (Ib)

A solution of 0.5 g NaOH in 10 mL CH_3OH was added with caution to a warmed solution of 6-(2-hydroxy-2-methylbut-3-ynyl)-2-(2-hydroxy-2-methylbut-3-ynylphenyl)-3-phenylquinoxaline (0.3 g, 0.67 mmol) in 825 mL toluene in a reaction vessel fitted with a distillation apparatus. The reaction mixture was distilled until 650 mL of distillate was collected and the remaining solution was evaporated to dryness. The residue was dissolved in 65 mL CH_2Cl_2, added to 150 mL water, and separated from the aqueous layer. The organic layer was washed two times with 100 mL water, concentrated to 50 mL, stirred with 8 g $MgSO_4$, filtered, and poured onto a column containing 68.38 g of silica gel. The product was eluted with CH_2Cl_2 and evaporated to dryness to yield 0.2 g (91%) mp 121°C, IR (neat) 3310 cm^{-1}(≡C-H); ^{1}HNMR ($CDCl_3$) δ 7.70 (m, 12H, Ar-H), 3.28 (s, 1H, C≡CH), 3.05 (s, (1H, C≡CH); ^{13}CNMR see Table 2. MS Calcd for $C_{24}H_{14}N_2$: M^+, 330. Found: M^+, 330. Anal. Calcd: C, 87.27; H, 4.24; N, 8.48. Found: C, 87.39; H, 3.84; N, 8.24.

TABLE 2

^{13}CNMR CHEMICAL SHIFTS[a] OF THE QUATERNARY CARBONS OF THE QUINOXALINE ISOMERS

Compounds							
IIa		IIb		Ia		Ib	
ppm	Carbon	ppm	Carbon	ppm	Carbon	ppm	Carbon
153.45	C-2	153.56	C-3	153.55	C-2	153.80	C-3
152.02	C-3	151.90	C-2	152.90	C-3	152.54	C-2
141.59	C-10	141.83	C-10	140.95	C-10	140.73	C-10
140.36	C-1"	140.49	C-1"	140.50	C-9	140.63	C-9
140.27	C-9	140.04	C-9	138.86	C-1"	138.80	C-1"
138.02	C-1'	138.01	C-1'	138.21	C-1'	138.13	C-1'
122.35	C-3"	122.38	C-3"	123.77	C-3"	123.85	C-3"
95.81	C-6	96.09	C-6	122.38	C-6	122.33	C-6

[a]Chemical shifts were measured from $CDCl_3$ and converted to the TMS scale using $CDCl_3$ - TMS= 76.91 ppm.

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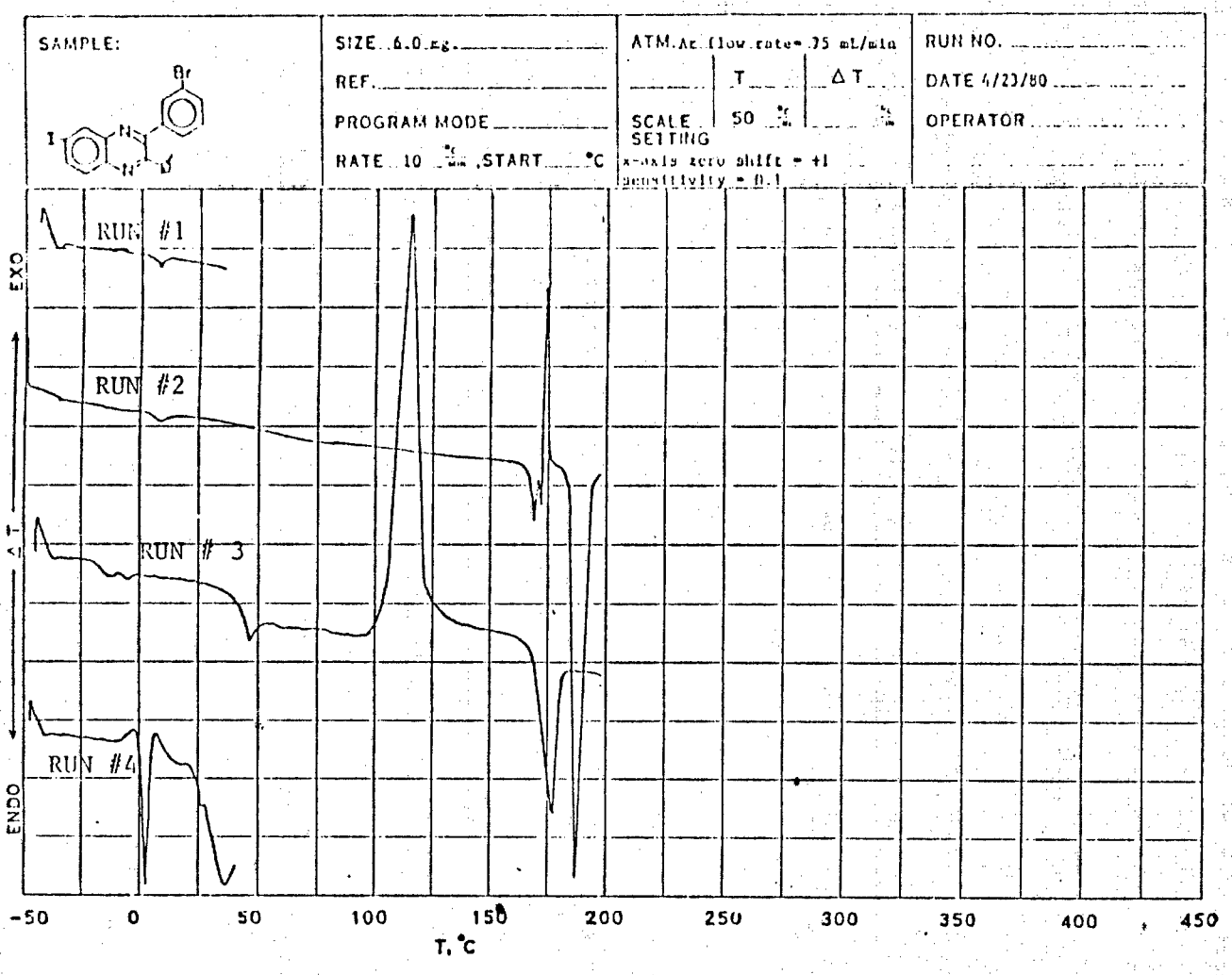

Figure 1. The Composite of Successive Partial DSC Scans of 3-(3-bromophenyl)-2-phenyl-6-iodoquinoxaline (IIa)

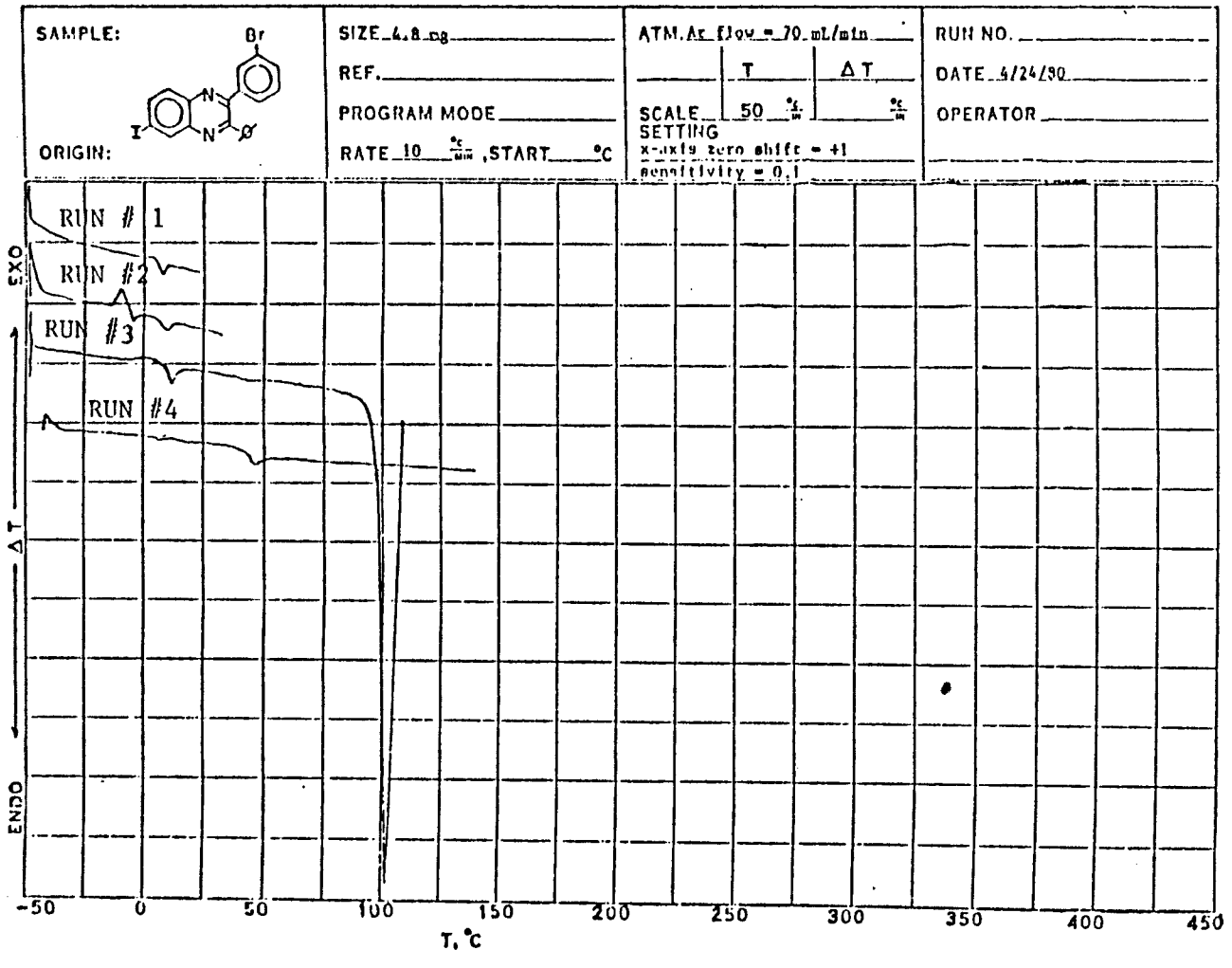

Figure 2. The Composite of Successive Partial DSC Scans of 2-(3-bromophenyl)-3-phenyl-6-iodoquinoxaline (IIb)

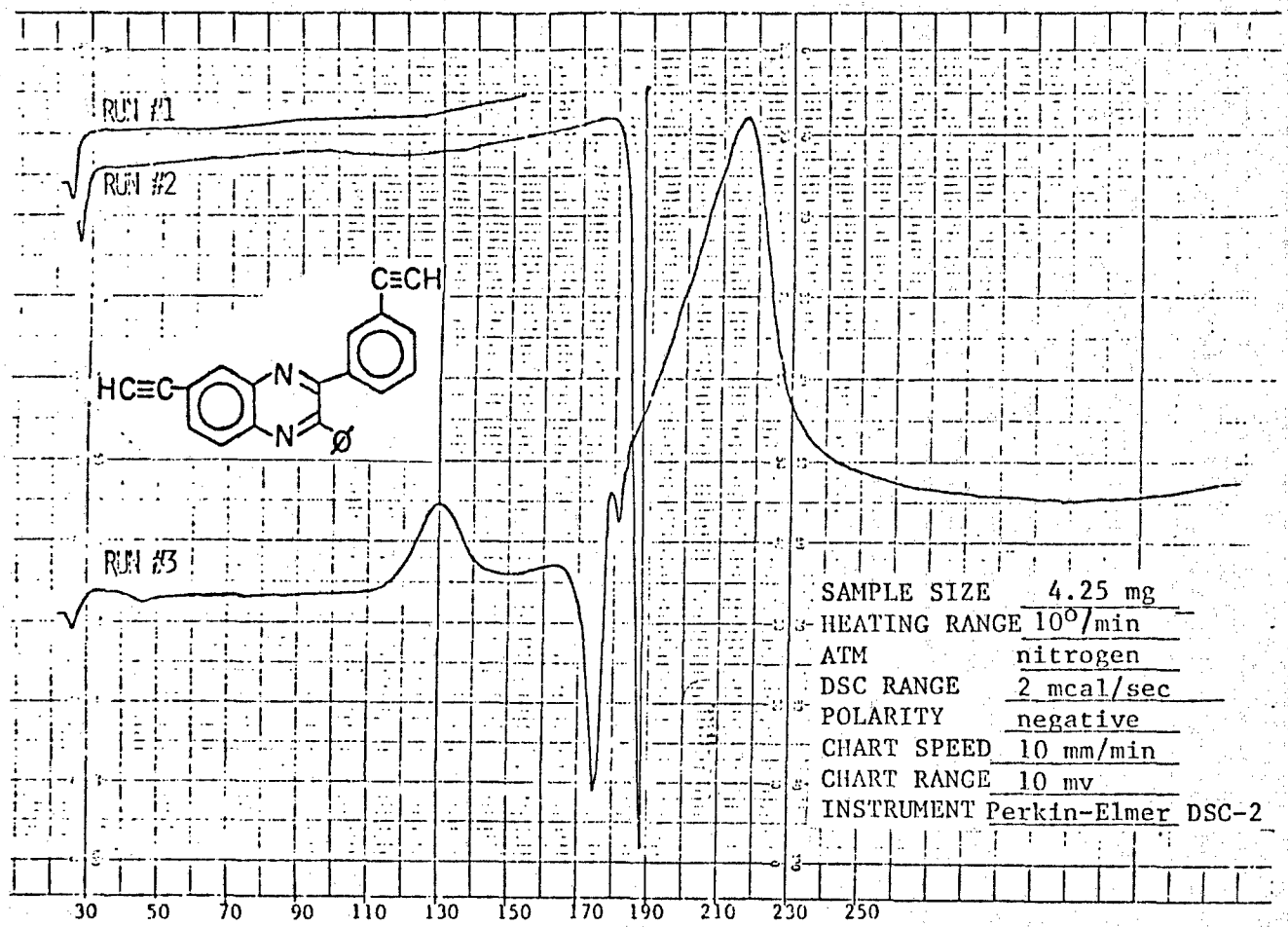

Figure 3. The Composite of Successive Partial DSC Scans of 6-ethynyl-3-(3-ethynylphenyl)-2-phenylquinoxaline Obtained Using the Perkin-Elmer DSC-2 (Ia)

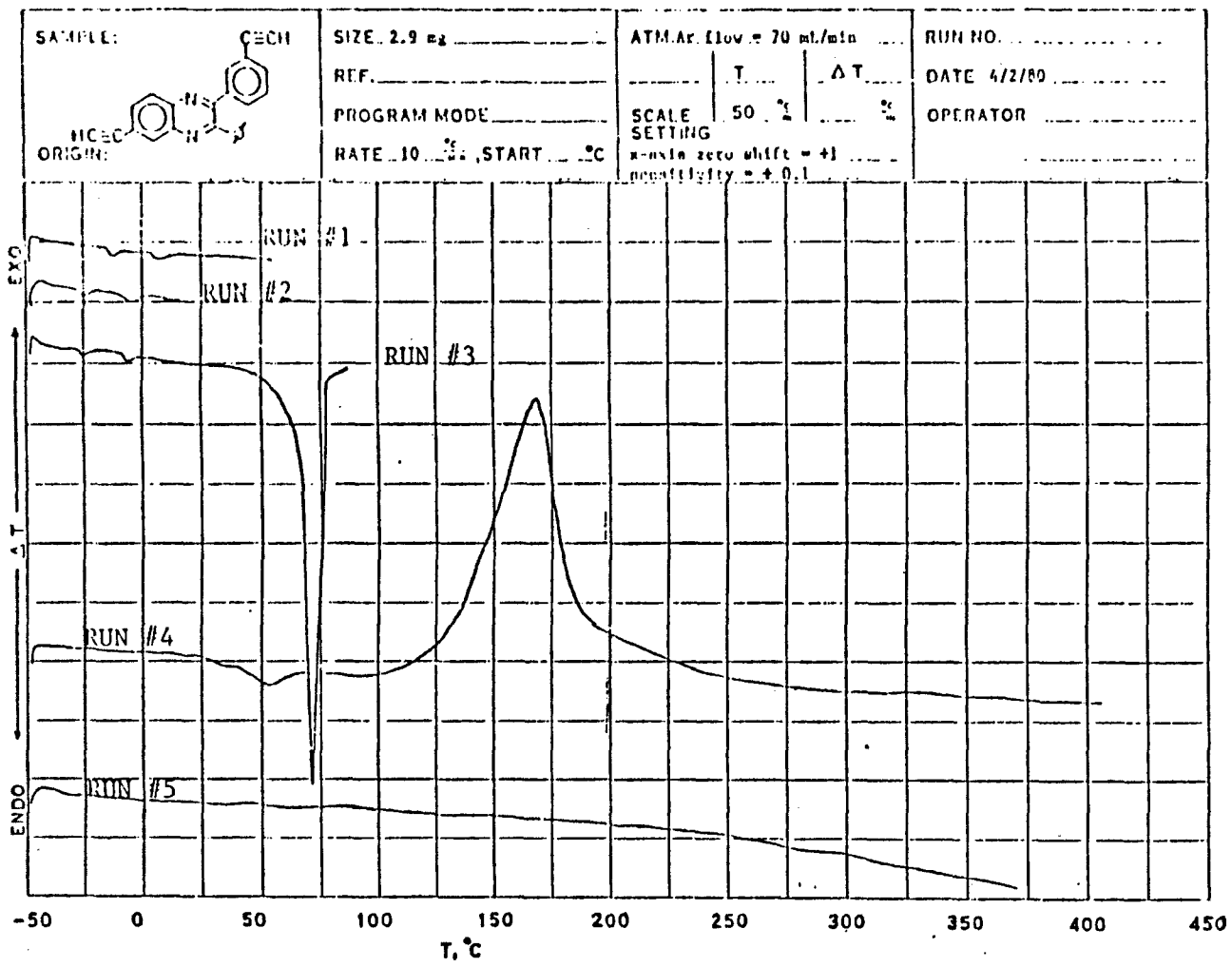

Figure 4. The Composite of Successive Partial DSC Scans of 6-ethynyl-2-(3-ethynylphenyl)-3-phenylquinoxaline (Ib)

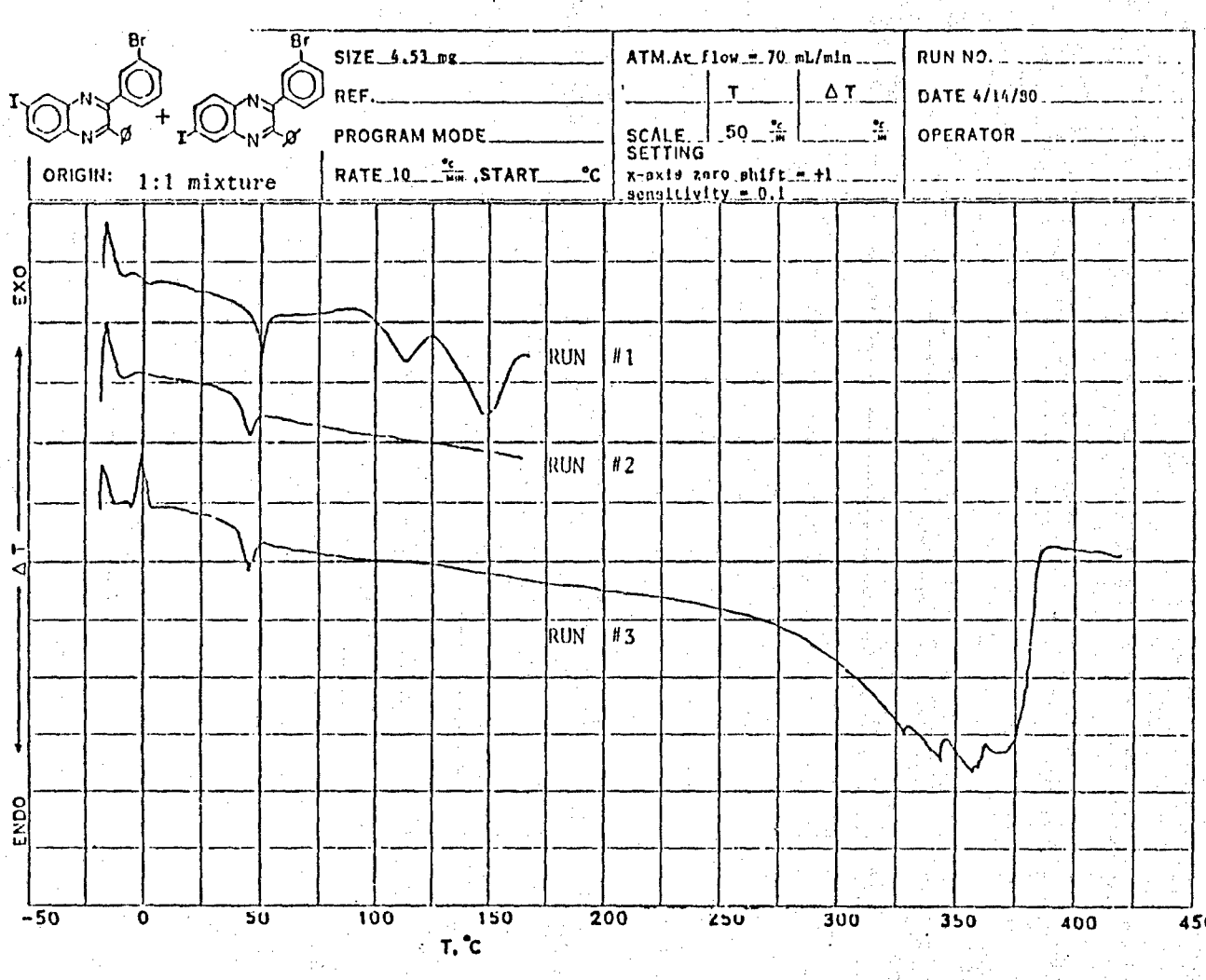

Figure 5. The Composite Partial DSC Scans of the 1:1 Mixture of 3-(3-bromophenyl)-2-phenyl-6-iodoquinoxaline and 2-(3-bromophenyl)-3-phenyl-6-iodoquinoxaline

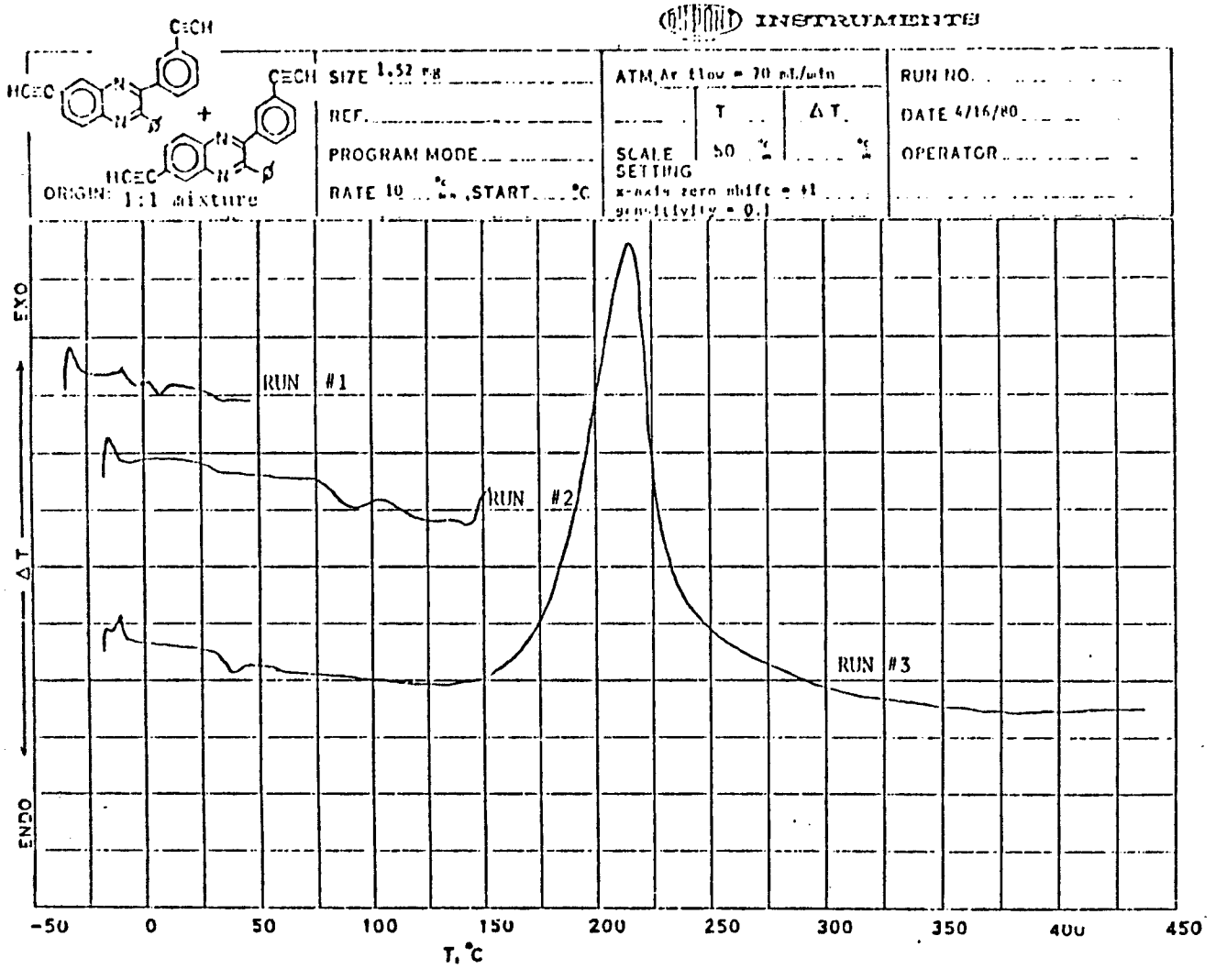

Figure 6. The Composite of Successive Partial DSC Scans of the 1:1 Mixture of 6-ethynyl-3-(3-ethynylphenyl)-2-phenylquinoxaline and 6-ethynyl-2-(3-ethynylphenyl)-3-phenylquinoxaline

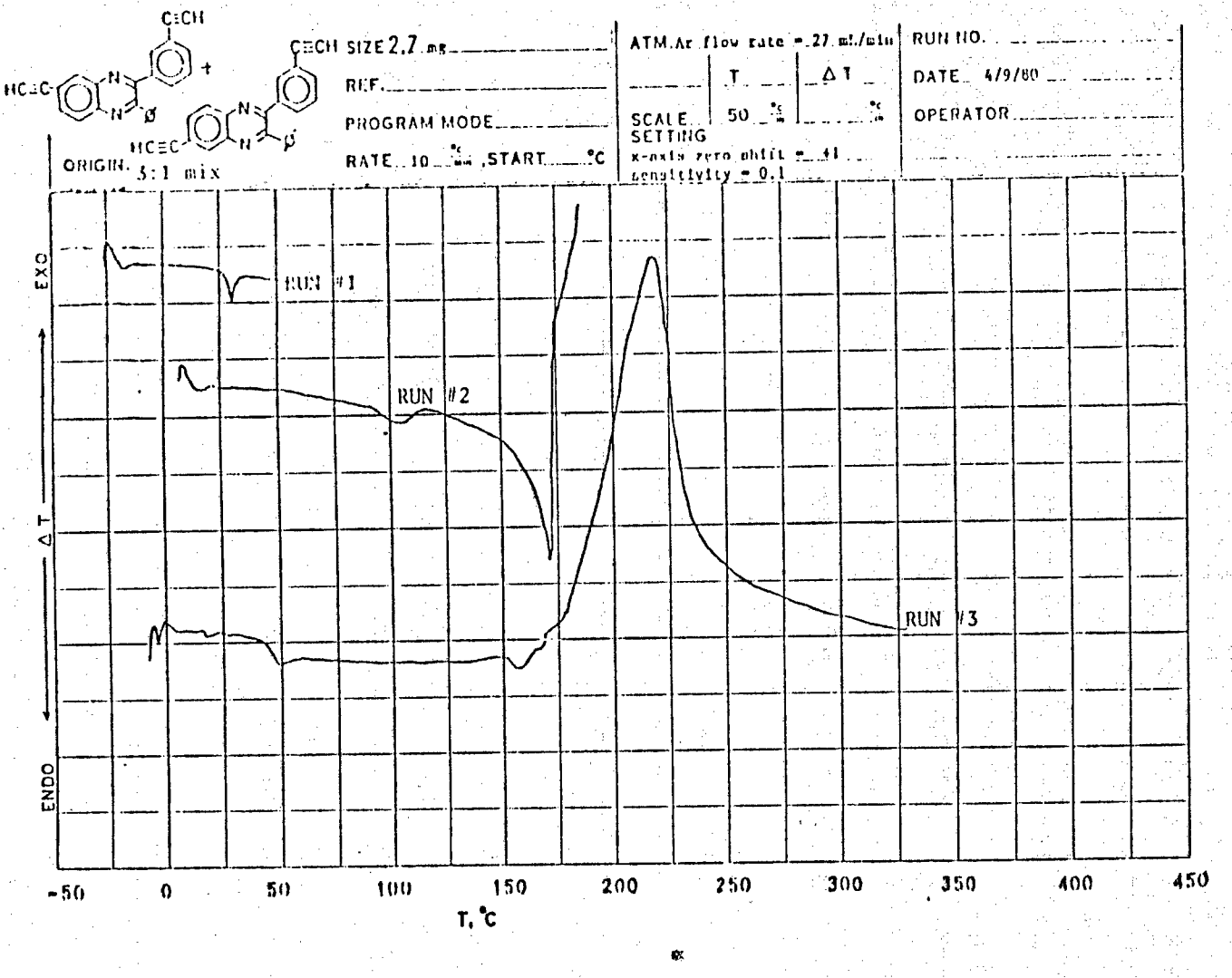

Figure 7. The Composite of Successive Partial DSC Scans of the 3:1 Mixture of 6-ethynyl-3-(3-ethynylphenyl)-2-phenylquinoxaline and 6-ethynyl-2-(3-ethynylphenyl)-3-phenylquinoxaline

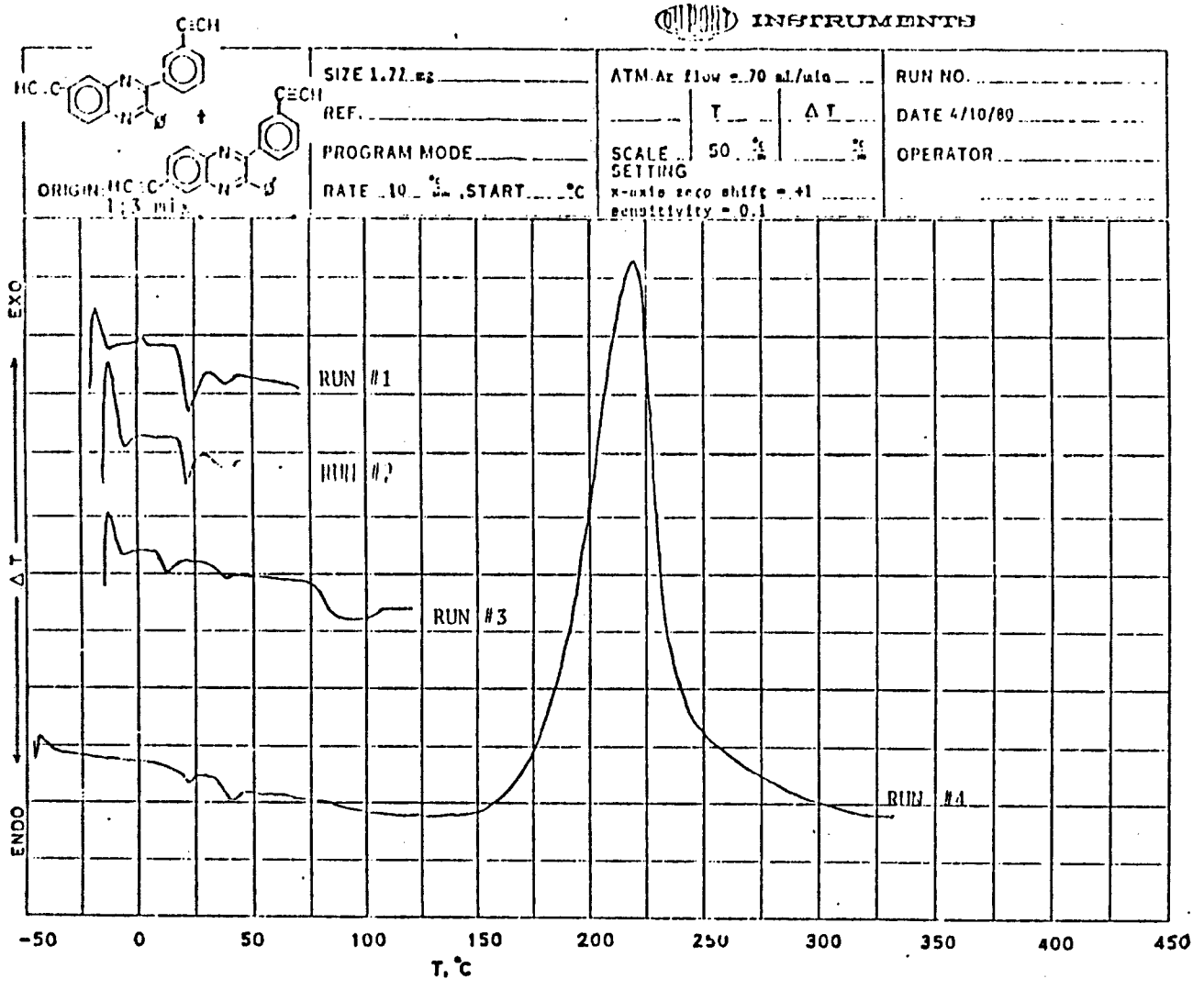

Figure 8. The Composite of Successive Partial DSC Scans of the 1:3 Mixture of 6-ethynyl-3-(3-ethynylphenyl)-2-phenylquinoxaline and 6-ethynyl-2-(3-ethynylphenyl)-3-phenylquinoxaline

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