amount of 6 M HCl (about 3 drops). The solution was carefully adjusted to pH 7 with 1 M NaOH, and the resulting mixture was filtered. The filtrate was reduced in vacuo to 2 mL and then cooled at 3 °C overnight. The resulting precipitate was collected by filtration and dried at 0.1 torr to afford a powder: dec >235 °C without melting; R_f 0.43 (solvent C); ^{1}H NMR (($(CD_3)SO/D_2O$) δ 1.65 (s, 3, CH_3, isomer 1), 1.75 (s, 3, CH_3, isomer 2), 3.95 (s, 2, CH_2, isomer 2), 4.40 (s, 2, CH_2, isomer 1), 6.00 (s, 1, C=CH, isomer 1), 7.15 (s, 1, C=CH, isomer 2), 7.70 (s, 1, imidazole CH, isomer 2), 7.80 (s, 1, imidazole CH, isomer 1); mass spectrum, m/e 218 (contaminant, 5), 203 (M^+), 201 ($M^+ - H_2$, base peak); high-resolution mass spectrum, calcd for $C_9H_9N_5O$ 203.0807, obsd 203.0802.

1,N^2-(2-Methylallylidene)guanine (7-Methyl-10-oxo-9,10-dihydropyrimido[1,2-a]purine) (3a). To a solution of the crude dihydro compound (15) in dry DMF as described earlier was added 150 mg of activated MnO_2[31] and the mixture was stirred at 55 °C under dry N_2. After 36 h, an additional 80 mg of MnO_2 was added and the progress of the reaction was followed by TLC using solvent C. The reaction was allowed to proceed for an additional 15 h after which TLC indicated that essentially all the starting material had been converted to a single fluorescent product. The mixture was filtered through Celite and the solid was washed with hot DMF (5 × 6 mL). The filtrate and washings were combined and evaporated in vacuo, and then the residue was dissolved in 10 mL of 1 M HCl and carefully adjusted to pH 7 with 2 M NaOH. The solution was evaporated to dryness and coevaporated with absolute MeOH (1 × 20 mL). The residue was extracted with hot absolute EtOH (2 × 20 mL), and then the extracts were combined and evaporated. The remaining solid was mostly dissolved in 3 mL of boiling EtOH, then 20 mL of petroleum ether was added protionwise with swirling, and the resulting precipitate was triturated. Cooling for 1 h at −10 °C followed by filtration and drying at 0.1 torr gave the product as a powder (44 mg, 53% based on 4). This material was compared with an authentic sample of the guanine–methylmalondialdehyde adduct[19] and was found to be identical by TLC in three systems (R_f 0.38, solvent A; 0.63, solvent B; 0.37, solvent C), mass spectrometry, UV, and "mixed" ^{1}H NMR.

Acknowledgment. This work was supported by Research Grant GM 05829 from the National Institutes of Health, U.S. Public Health Service. High-resolution and field-desorption mass spectral data were obtained in part under a grant from the National Institute of General Medical Sciences (GM 27029). We thank M. d'Alarcao and Dr. M. Hinterberger for their valuable suggestions during the course of this work.

Registry No. 3a, 57325-61-8; **4**·HCl, 75993-48-5; **5**, 75993-49-6; **9**, 36056-90-3; **10**, 75993-50-9; **11**, 75993-51-0; **12**, 10333-88-7; **13**, 75993-52-1; **13** picrate, 75993-53-2; **14**·HCl, 75993-54-3; **15** (isomer 1), 75993-55-4; **15**·HCl (isomer 1), 75993-56-5; **15** (isomer 2), 75993-57-6; **15**·HCl (isomer 2), 75993-58-7.

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[31] The sample was a gift from the Carus Chemical Co., LaSalle, IL, through Mr. Lyle Wright.

A ^{13}C NMR Method To Determine the Origin of Cross-linked Chloromethyl Polystyrenes Used in Polymer-Supported Synthesis[1]

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Chloromethyl polystyrene cross-linked with 1–2% divinylbenzene is the most commonly used support for solid-phase peptide synthesis, polymer-bound organic synthesis, polymer-bound transition metal complex catalysis, and polymer-bound phase-transfer catalysis. Most researchers obtain chloromethyl polystyrene from commercial sources because the common chloromethylating reagent, chloromethyl methyl ether (and its unavoidable contaminant bis(chloromethyl) ether), is a potent cancer-suspect agent. Chloromethyl polystyrene could be made by chloromethylation of cross-linked polystyrene under a wide variety of conditions (Lewis acid, solvent, temperature, time) or by copolymerization of styrene, divinylbenzene, and chloromethylstyrene, yet suppliers usually do not inform customers about the manufacturing processes for their products. We report here a method that enables one to identify whether such material was prepared by the chloromethylation method or the copolymerization method.

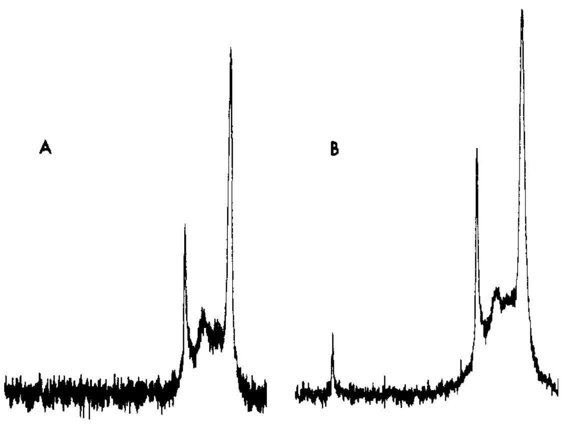

Figure 1. (A) $^{13}C[^1H]$ NMR spectrum of aliphatic carbon atoms of polymer 1. Peak assignments are as follows: ipso aromatic, 145.2 ppm; ortho and meta, 127.6; para, 125.5; CH_2Cl, 46.3; backbone CH, 40.3; backbone CH_2, 40–47. (B) $^{13}C[^1H]$ NMR spectrum of polymer 5, Bio-Beads SX-1 chloromethylated, 1.19 mmol of Cl/g, control no. 14137. The small peak at 65.1 ppm is due to CH_2OH, which arises from partial hydrolysis of chloromethyl groups during manufacture.

Table I lists composition, ^{13}C NMR line widths of polymer gels swelled in $CDCl_3$, and weight percent polymer of gels swelled in chloroform and in toluene. Five samples were prepared by us, and three were from commerical sources. The notable differences in ^{13}C NMR spectra of polymers with the same nominal degree of cross-linking are that poly(styrene-*co*-(chloromethyl)styrene) has narrower backbone methine carbon line widths and wider chloromethyl carbon line widths than those of chloromethylated polystyrene. A typical ^{13}C NMR spectrum appears in Figure 1. The greater line width of the chloromethyl carbon in poly(styrene-*co*-(chloromethyl)styrene) is due to the use of an approximately 60:40 mixture[2] of *m*- and *p*-(chloromethyl)styrene in copolymerization compared with the >90% para selectivity expected in chloromethylation of polystyrene with Lewis acids.[3] Although the meta and para isomer peaks are not resolved in 25.2-MHz ^{13}C NMR spectra of gel polymers, the isomeric mixture gives wider lines. The greater line widths of backbone methine carbon peaks of chloromethylated polystyrenes are probably due to methylene cross-linking introduced during the chloromethylation process. Chloromethylation of soluble, uncross-linked polystyrene carried to high conversion produces insoluble polymer.[4]

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[1] Supported by the U.S. Army Research Office.

[2] Dow Chemical Co., product specifications for vinylbenzyl chloride.

[3] Olah, G. A.; Tolgyesi, W. S. In "Friedel-Crafts and Related Reactions"; Olah, G. A., Ed., Wiley-Interscience: New York, 1964; Vol. 2, pp 659–784.

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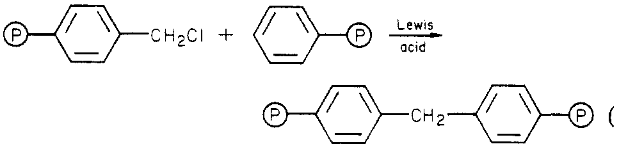
Table I. **Properties of Cross-linked Poly(styrene-*co*-(chloromethyl)styrene) and Chloromethylated Polystyrene**

polymer	mol % divinylbenzene[a]	mol % chloromethyl residues[b]	^{13}C line width, Hz, in $CDCl_3$		wt % polymer	
			CH	CH_2Cl	$CHCl_3$[c]	toluene[d]
		poly(styrene-*co*-(chloromethyl)styrene)				
1	0.87	18.6	16	11.5	10	18
2	1.64	9.0	27	*e*	23	34
3	1.76	19.0	22.5	16	17	31
4	1.87	41	27	16	20	30
		chloromethylated polystyrene				
5	0.80	13.2	20.5	8	14	23
6	1.66	7.6	25	*e*	16	27
7	1.61	44	35	9	19	33
8	1.55	46	37	10.5	22	35

[a] All samples are nominally 1% or 2% divinylbenzene by weight. [b] Calculated from monomer composition of copolymerization or from Cl content of chloromethylated polystyrene. [c] ±3%. [d] ±2%. [e] Too small to measure.

Similarly, intrapolymer alkylation of a previously cross-linked polystyrene causes secondary crosslinking and decreases the mobility of its polymer chains (eq 1). The reduced mobility accounts for the wider ^{13}C lines for the polymer backbone of chloromethylated polystyrene.



(1)

The methine carbon line width is a measure of the effective degree of cross-linking of a chloromethyl polystyrene. Cross-linking of the samples in Table I increases in the order 1 < 5 < 2, 3, 4, 6 < 7, 8. Chloromethylated resin 5 is more cross-linked than copolymer 1, yet both contain 1% divinylbenzene. Chloromethylated resins 6, 7, and 8 have increasing methine carbon line widths due to increasing amounts of secondary cross-linking, and 7 and 8 are more cross-linked than 3 and 4, which also contain 2% divinylbenzene. The degree of cross-linking also affects the CH_2Cl line width. One must first estimate the effective cross-linking from the methine carbon line width before using the CH_2Cl line width as a criterion for the meta/para isomer content and the origin of the cross-linked chloromethyl polystyrene. This analysis is valid only for copolymers containing ≥13 mol % chloromethyl residues (≥1.2 mmol of Cl/g of dry resin) for two reasons. (a) A sizeable CH_2Cl peak in the NMR is needed to measure its line width. (b) Substantial chloromethylation is needed for the secondary cross-linking to broaden the backbone methine carbon resonance. Note that polymers 2 and 6 are not distinguishable, but the line widths distinguish clearly 1 from 5 and 3, and 4 from 7 and 8.

Another test often used qualitatively to determine the extent of cross-linking of polymers is swelling in good solvents. The swellings in chloroform and toluene in Table I show no difference between chloromethylated polystyrene and poly(styrene-*co*-(chloromethyl)styrene) within experimental error, although the degree of swelling decreases (weight percent of polymer increases) as the mole percent of (chloromethyl)styrene repeating units increases. Clearly the ^{13}C NMR line widths provide a more sensitive test than do polymer swellings for the origin of cross-linked chloromethyl polystyrenes.

Subtle differences in polymer chain mobility under swollen conditions and in the meta/para isomer distribution of functional groups on chloromethyl polystyrenes may affect the results of polymer-bound synthesis and catalysis experiments. The ^{13}C NMR line widths sould enable researchers in these fields to learn about the histories and to exercise better control over the quality of their polymer samples.[5]

Experimental Section

Commercial Polymers. 5: Bio-Beads SX-1 chloromethylated, 1.19 mmol of Cl/g, Bio-Rad Laboratories. **6:** Merrifield polymer, 2% cross-linked, 0.7 mmol of Cl/g, Fluka. **7:** Merrifield polymer, 2% cross-linked, 3.5 mmol of Cl/g, Fluka.

Poly(styrene-*co*-(chloromethyl)styrene) (3). A solution of 1.35 g of gelatin, 12.3 g of poly(diallyldimethylammonium chloride) (Calgon Corp., Cat-Floc T), and 5.1 g of boric acid in 450 g of water adjusted to pH 10.0 with 25% aqueous sodium hydroxide and added to a 1000-mL round-bottom flask fitted with reflux condenser, mechanical stirrer, and thermocouple connected to a proportional temperature controller (Love Controls Corp., Model 49). A solution of 214 g of styrene (Aldrich), 75 g of (chloromethyl)styrene (Dow, 60/40 meta/para), 10.9 g of technical 55% divinylbenzene (Polysciences), and 1.5 g of azobis(isobutyronitrile) (Aldrich) was added. No attempt was made to remove polymerization inhibitors from the monomers. The flask was purged with nitrogen for 30 min, and a nitrogen atmosphere was maintained throughout polymerization. The mixture was heated with stirring to 70 °C for 17 h. Insoluble polymer beads were collected on sieves and washed thoroughly with water. Polymers 1, 2, and 4 were made by the same procedure.

Chloromethylated Polystyrene (8). A sample of 104 g of 2% divinylbenzene-cross-linked polystyrene was stirred in 265 mL of chloromethyl methyl ether (**Caution**: cancer-suspect agent)[6] and 400 mL of 1,2-dichloropropane at 10 °C for 60 min. Solid anhydrous zinc chloride, 109 g, was added, and the mixture was stirred for 5.5 h at 10 °C. The reaction mixture was quenched by cautious addition of methanol, and excess liquid was decanted. The solid polymer was washed with five portions of water, one portion of saturated aqueous sodium bicarbonate, and two portions of water. Excess liquid was decanted each time. Reaction of a small portion of the polymer with a tenfold excess of trimethylamine in 75/25 v/v dichloromethane/methanol at 25 °C for 3 h gave an anion-exchange resin that contained 2.95 mequiv of Cl^-/g. Assuming complete reaction with trimethylamine, the chloromethylated polystyrene contained 3.6 mmol of Cl/g.

^{13}C NMR Spectra. Each polymer, 3–10 g, was washed in a column with 500 mL of 90/10 w/w tetrahydrofuran/concentrated aqueous HCl and 250 mL of methanol to remove possible residual monomer, uncross-linked polymer, and metal salts. Samples were dried to constant weight under vacuum at room temperature. Each polymer was swollen in $CDCl_3$ in a 12-mm NMR tube. ^{13}C and ^{1}H spectra were recorded at 25.2 MHz on a Varian XL-100-15

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(5) ^{13}C NMR spectra of some commercial chloromethylated polystyrenes used in solid-phase peptide synthesis also show a sizeable peak for hydroxymethyl groups: Manatt, S. L.; Horowitz, D.; Horowitz, R.; Pinnell, R. P. *Anal. Chem.* **1980**, *52*, 1529. We thank Dr. Manatt for informing us of these results prior to publication.

(6) This experiment was carried out in a hood that meets OSHA standards for handling classified carcinogens. We strongly discourage use of chloromethyl methyl ether in most research laboratories. For a leading reference on correlation between chloromethyl methyl ether exposure and lung cancer, see: Weiss, W. *J. Occup. Med.* **1976**, *18*, 194–199.

and ^1H spectra were recorded at 25.2 MHz on a Varian XL-100-15 instrument equipped with a Nicolet TT-100 pulsed Fourier transform unit. Typical conditions were 8K data points, 90° pulse, 1.36-s acquisition time, zero delay, 5000–15 0000 acquisitions, 0.2-Hz exponential multiplier, 6000-Hz sweep width, 30 °C. Line widths at half-height were measured on 1000-Hz sweep-width expansions of the original spectra. A line drawn across tops of backbone CH_2 resonances was used as baseline for the CH_2Cl peak.

Swelling of Cross-linked Polymers. A 0.2-g sample of dry polymer was carefully weighed in a fritted-glass tube and soaked at least 2 h in $CHCl_3$ or toluene. The fritted tube was placed in a polyethylene centrifuge tube and centrifuged until all adhering solvent droplets were removed (5–10 min). The sample was reweighed to determine the weight percent of polymer. All experiments were performed at least twice. Estimated errors with $CHCl_3$ are greater than those with toluene because $CHCl_3$ evaporates from the polymer beads at a slow rate even after excess droplets are removed.

Registry No. Styrene, chloromethylstyrene, divinylbenzene copolymer, 55844-94-5; divinylbenzene, styrene copolymer, 9003-70-7.

Excited-State Properties of *cis*- and *trans*-1,2-Di(9-anthryl)ethylenes

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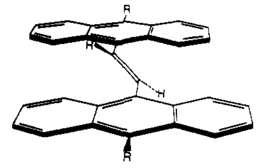
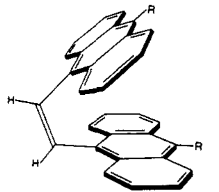
Steric impairment of conjugation in 1,2-diarylethylenes is known to contribute to the different photochemical and photophysical properties which may distinguish geometrical isomers.[1,2] For example, sterically unhindered *trans*-stilbene shows fine structure in its absorption spectrum and, characteristically, its fluorescence spectrum exhibits a small Stokes shift as differences between ground-state and excited-state geometry are small. In *cis*-stilbene, by comparison, the hypsochromically shifted absorption spectrum is less intense and less structured due to steric interaction of the aromatic hydrogens in the ortho positions. Moreover, because of the reduced lifetime in its excited singlet state, *cis*-stilbene in solution at room temperature is nonfluorescent. At 77 K in rigid media, however, the fluorescence quantum yield of *cis*-stilbene is as high as 0.75.

We report here on the excited state properties of *trans*- and *cis*-1,2-di(9-anthryl)ethylenes 1 and 2. Their respective geometries are intriguing inasmuch as neither one of the two geometrical isomers can assume a ground-state conformation in which the two anthracene systems are coplanar with the central ethylene bond. Inspection of Dreiding molecular models suggests that *trans*-1,2-di(9-anthryl)ethylenes 1 may alleviate intramolecular hydrogen interaction by deviation from planarity brought about by twists of about 50° around the two aryl–ethylene single bonds. In the resulting conformer, the two anthracene systems are alligned parallel as shown in 1. Steric relief can also be achieved by twists around the single bonds in mutally opposite directions so as to give a conformer in which the planes of the two anthracene systems would be in perpendicular arrangement. Accordingly, the electronic absorption spectra of *trans*-1,2-di(9-anthryl)ethylenes show little fine structure and only small bathochromic shifts relative to the absorption spectra of the correspondingly substituted 1,2-di(9-anthryl)ethanes, and in comparison to those of di(9-anthryl)acetylenes (see Figure 1).[3-5]



1

a: R = H
b: R = $OCOCH_3$
c: R = OCH_3



2

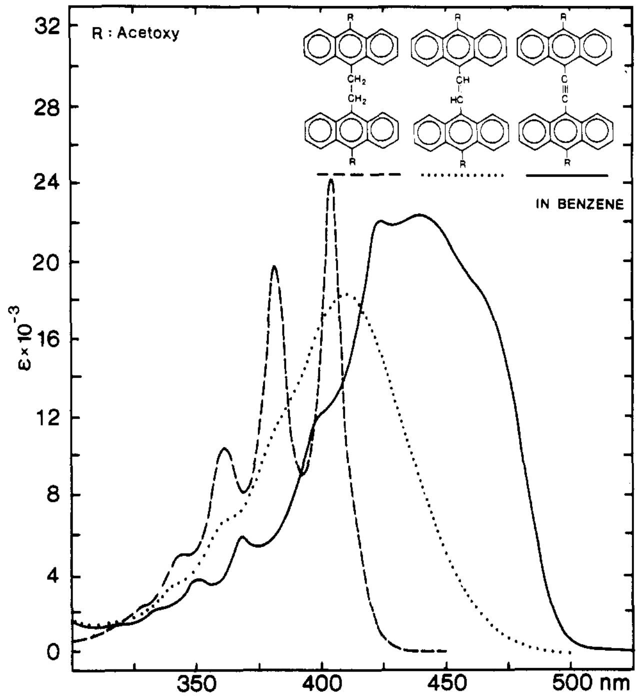


Figure 1. Electronic absorption spectra of 1,2-bis(10-acetoxy-9-anthryl)ethane (dashed curve), *trans*-1,2-bis(10-acetoxy-9-anthryl)ethylene (dotted curve), and bis(10-acetoxy-9-anthryl)-acetylene (solid curve) in benzene solution.

cis-1,2-Di(9-anthryl)ethylenes 2, apparently, have not been described heretofore.[6] Stereochemical considerations suggest that the planes of their two anthracene systems on one hand and the plane of the ethylene bond on the other hand may be in a mutually perpendicular arrangement. Consequently, the two anthracene moieties would face each other in relatively rigid geometry.

Using conventional fluorescence spectrometry, we find that *trans*-1,2-di(9-anthryl)ethylene (**1a**),[7] contrary to an earlier report,[8] actually is fluorescent in solutions at room temperature. Likewise, substituted[4] *trans*-1,2-di(9-anthryl)ethylenes **1b** and **1c** are found to be luminescent in solution at room temperature. Remarkably, in every case the broad, structureless luminescence is characterized by a gap of about 10 000 cm^{-1} between absorption and

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[1] (a) Fischer, G.; Seger, G.; Muszkat, K. A.; Fischer, E. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1569. (b) Goedicke, Ch.; Stegemeyer, H.; Fischer, G.; Fischer, E. *Z. Phys. Chem. N. F.* **1976**, *101*, 181. (c) Fischer, E. *J. Phys. Chem.* **1980**, *84*, 403. (d) Sharafy, Sh.; Muszkat, K. A. *J. Am. Chem. Soc.* **1971**, *93*, 4119.

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