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Investigation of the Polymerization of 1,4-Dinitrosobenzene by Low-Temperature Infrared and UV Absorption Spectroscopy

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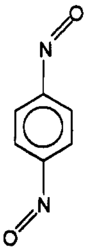
ABSTRACT: Warming poly(1,4-phenyleneazine *N,N*-dioxide) at 50–65 °C and depositing under vacuum onto a CsI window at cryogenic temperatures gives 1,4-dinitrosobenzene, identified from infrared bands around 1520, 1120, 850, and 780 cm^{-1}, which are characteristic for aromatic *C*-nitroso compounds. Thin films of 1,4-dinitrosobenzene were warmed from 32 K to room temperature in vacuo, and the polymerization reaction was shown to proceed through an intermediate, stable from 180 to 220 K. The intermediate shows *C*-nitroso- vibrational frequencies similar to those of the monomer but also has a strong band at 1260 cm^{-1} typical for an O–N=N–O vibration in its infrared spectrum, assigned to the trans dimer of 1,4-dinitrosobenzene. Further warming of these films above 220 K results in formation of oligomers, and finally at temperatures from ca. 260 K to room temperature, complete polymerization occurs to regenerate poly(1,4-phenyleneazine *N,N*-dioxide). Similar results were obtained from UV absorption spectroscopy, which detected formation of an intermediate at ca. 180 K that on further warming to room temperature gave the polymer.

Introduction

C-Nitroso compounds generally exist as azine dioxide dimers in the solid state which can be converted into monomers by heating, by photolysis, or by dissolution to high dilution.[1,2] A few *C*-nitrosoarenes with electron-donating groups in the *para* position can exist as stable monomers; for example, 4-(dimethylamino)nitrosobenzene is a stable monomer in the solid state.[1] Because of the tendency for *C*-nitroso compounds to react with themselves, dinitroso compounds are unstable. For example, while 1,2-dinitrosobenzene is known, it is stable only up to ca. 80 K, at which point it cyclizes to form benzofuroxan.[3] Similarly, 1,4-dinitrosobenzene is not isolable and exists as poly(1,4-phenyleneazine *N,N*-dioxide) at room temperature.[4–6] This polymer is of particular interest because it can be used in a solventless, laser-imageable resist process.[7] In this paper the first isolation of 1,4-dinitrosobenzene in argon and as a film at cryogenic temperatures and its subsequent polymerization upon warming to room temperature are reported.

Results and Discussion

A. IR Spectroscopy. Poly(1,4-phenyleneazine *N,N*-dioxide) was heated to 50–60 °C, and the vapor was cocondensed with a stream of argon onto a CsI window cooled to 32 K. The infrared spectrum of the condensate (Figure 1a) has the characteristic sharp bands of a monomeric matrix-isolated species. The absence of strong bands at 1350–1400 cm^{-1}, due to the cis-O–N=N–O stretch, and 1248–1285 cm^{-1}, due to the trans-O–N=N–O stretch, and the absence of bands due to the polymer suggest that the isolated species is 1,4-dinitrosobenzene.[1,8,9] The strong bands around 1530, 1110, and 780 cm^{-1}, due to N=O and C–N vibrations, are typical of aromatic *C*-nitroso compounds, and the overall spectrum is very similar to that of 1,2-dinitrosobenzene in argon at 14 K (Figure 1b).[1,3,8,10] Gas-phase infrared spectroscopic studies on nitrosobenzene have led to the assignment of bands at 1523 cm^{-1} to the N=O stretch, at 1112 cm^{-1} to the C–N stretch, and at 812 cm^{-1} to the C–N stretch and ring deformation.[8] A striking feature of the infrared spectrum of 1,4-dinitrosobenzene matrix-isolated in argon is that the bands associated with the *C*-nitroso vibrations all appear as doublets (1534, 1529 cm^{-1}, N=O stretch; 1113, 1110 cm^{-1}, C–N stretch; 780, 762 cm^{-1}, C–N stretch) and are assigned to rotamers 1 and 2: The doublets for the C–N=O bands are not merely due to "matrix effects" such as monomer isolated in two different sites because other bands should also appear as doublets. Furthermore, the bands reported for the same vibrations in nitrosobenzene, which cannot exist as two rotamers, exhibit no splitting in argon matrices under similar conditions.[10] However, the N=O stretching frequency of 1,2-dinitrosobenzene, which can exist as three different conformers, is very broad due to the superimposition of the three stretching frequencies at 1530 cm^{-1}.[3] Clearly resolved bands for a similar molecule, phthalaldehyde, which can exist as three rotational isomers in nitrogen matrices at cryogenic temperatures, have been reported.[11]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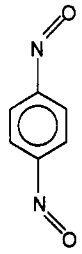
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To study the polymerization reaction, a thin film of 1,4-dinitrosobenzene was deposited in the absence of argon under similar conditions. The infrared spectrum of the film (Figure 2a) is very similar to that of the matrix-isolated sample except that the bands are broadened, typical for an aggregated monomeric species. The doublets due to the rotational isomers 1 and 2 are no longer resolved due to the broadness of the IR bands of the film. In preliminary experiments thin films of 1,4-dinitrosobenzene were warmed, and the final IR spectrum recorded at room temperature (Figure 2b) shows loss of the *C*-nitroso stretching frequency at 1530 cm^{-1} and a new very strong band at 1265 cm^{-1}, consistent with the trans-O–N=N–O

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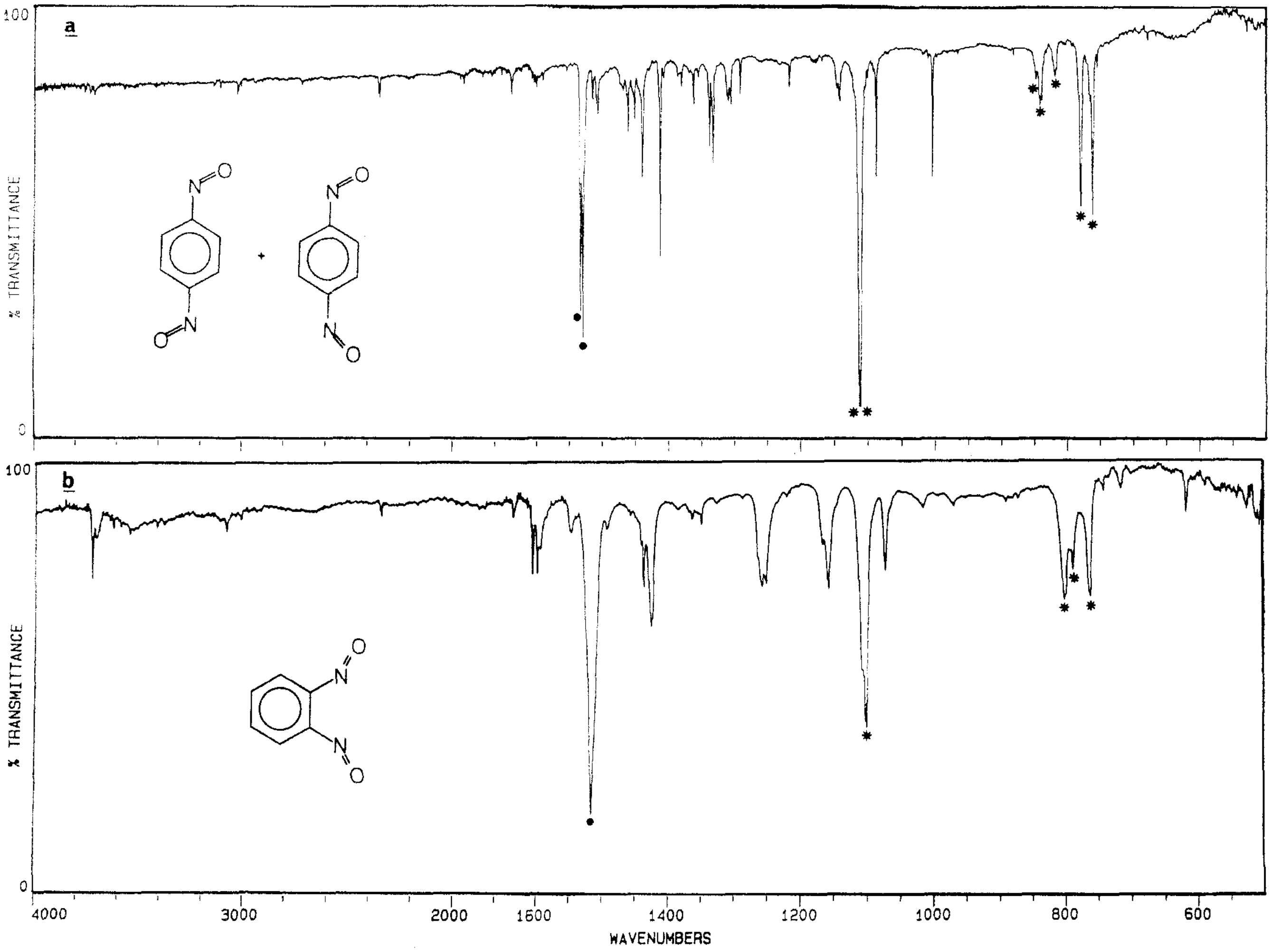
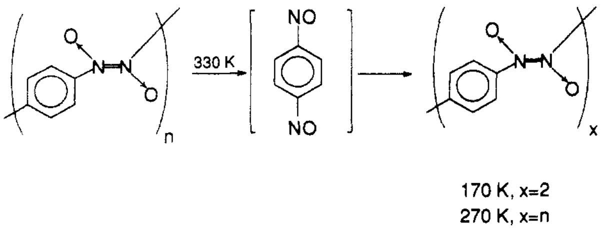


Figure 1. IR spectra recorded in argon at 14 K: (a) 1,4-dinitrosobenzene; (b) 1,2-dinitrosobenzene. All spectra are recorded in transmittance. Bands marked with a solid circle are N=O stretch, and bands marked with an asterisk are C–N=O vibrations. (Note scale change at 1600 cm^{-1}.)

frequency. The spectrum had bands at 3111, 1486, 1418, 1308, 1265, 1104, 1012, 859, 777, 570, and 485 cm^{-1}, which agree very well with those recently reported by Gowenlock (1481, 1411, 1304, 1265, 1100, 1010, 860, and 780 cm^{-1}) for poly(1,4-phenyleneazine *N,N*-dioxide).[6] From these preliminary experiments it was found that the spectrum of 1,4-dinitrosobenzene was virtually unchanged in warming from 32 K to ca. 150 K, but at ca. 200 K the C–N=O 1530-cm^{-1} band decreased in intensity and a strong new band at 1265 cm^{-1} due to an O–N=N–O vibration had formed. Finally, at 260 K the C–N=O vibration had disappeared, and the IR spectrum was almost completely that of the polymer.



In further experiments with more controlled heating from 32 K to room temperature it was found that while some band intensities changed, bands broadened or shifted ca. 5 cm^{-1} upon warming from 32 to 160 K; no new bands appeared. Thus only physical changes, such as relaxing of the matrix or interconversion between rotamers 1 and 2, occurred at temperatures below 160 K. However, dramatic changes in the IR spectra occurred upon heating from 170 to 176 K. The intensity of the C–N=O band at 1520 cm^{-1} decreases, and a new intense band, assigned to O–N=N–O, grew at 1260 cm^{-1} along with new bands at 1104, 860, 775, 579, and 570 cm^{-1}. Figure 3a shows the infrared spectrum from 1550 to 1050 cm^{-1} at 160 K, where all the bands are assigned to the monomer. Figure 3b shows the changes in the infrared spectrum recorded while heating the same sample from 170 to 176 K, where the absorbances of the C–N=O bands at 1530 and 1110 cm^{-1} decrease to 25–40% of their original intensities recorded at 160 K and a strong new band around 1260 cm^{-1} grows in. This dramatic change at 170 to 176 K is most likely to be dimerization or formation of a stable oligomer as there are isosbestic points for interconversion of the major bands, suggesting a simple A → B transformation. Also the same spectrum persists with only minor changes upon heating from 176 to 210 K. Particularly interesting is that the band at 1260 cm^{-1} is consistent with the O–N=N–O stretch for the trans isomer; the only band in the 1350–1400-cm^{-1} range expected for the cis-O–N=N–O stretch was a weak vibration at 1386 cm^{-1} that was present in the monomer spectrum. Thus randomly oriented monomer undergoes a stereoselective dimerization reaction at 170 K. At temperatures above 210 K the bands assigned to the C–N=O vibrations decrease in intensity while the O–N=N–O band grows; the final completion of polymerization occurs from 230 to 280 K. Figure 3c shows the infrared spectrum recorded at 280 K, where there are no traces of the C–N=O bands and the polymerization is complete. Figure 4 shows the growth and decay characteristics versus temperature for the major bands assigned

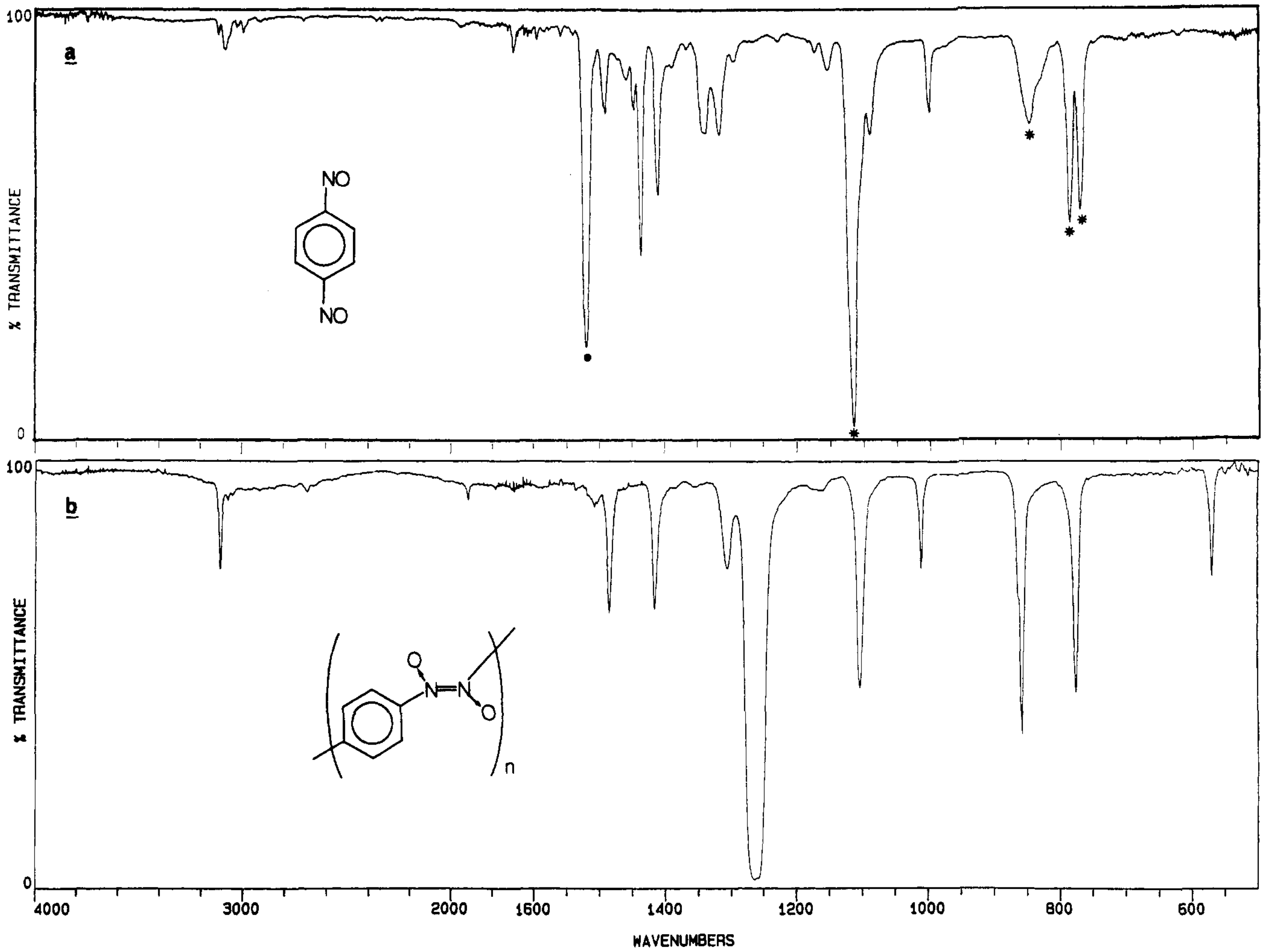


Figure 2. IR spectra: (a) 1,4-dinitrosobenzene (thin film), 14 K; (b) after warming to room temperature, poly(1,4-phenyleneazine *N,N*-dioxide).

Table I. IR Bands (cm^{-1}) Recorded for Dinitrosobenzenes, Dimer, and Polymer

1,2-dinitrosobenzene (Ar)	1,4-dinitrosobenzene (Ar)	1,4-dinitrosobenzene (film)	dimer	polymer
3108	3135	3118	3109	3111
3078	3100		3092	
			3076	3073
3064	3018	3085	3053	3050
3031	3012	3031	3030	
3009	3001	3000	2996	
	2938	2926		
1516	1534, 1529	1523	1526	
			1509	
	1507	1494	1486	1486
	1461	1459	1463	
	1451	1447	1448	
1435	1439	1437	1437	
1424	1413	1411	1417, 1411	1418
	1386, 1380	1386	1387	
	1338	1342	1343	
	1333	1336		
	1310, 1305	1316	1316	1308
1258, 1251	1292	1293	1257	1265
1166		1172		
1158	1145, 1142	1153		
1108, 1103, 1101	1113, 1110	1118	1117, 1104, 1092	1104
1074	1088	1092	1092	
			1012	1012
	1004	1002	998	
	849, 843, 841	848	861	859
804	820, 817		850	
790	780	786	783, 776, 769	777
765	762	771	579, 570	570
620	481	487	486	485

to the monomer and polymer. The dramatic transition at 170 K is observed for all the IR bands. Also some bands are not observed in 1,4-dinitrosobenzene or the polymer but are observed during the polymerization and are probably due to the growing oligomer, e.g., 1509, 775, 579, etc. (Table I).

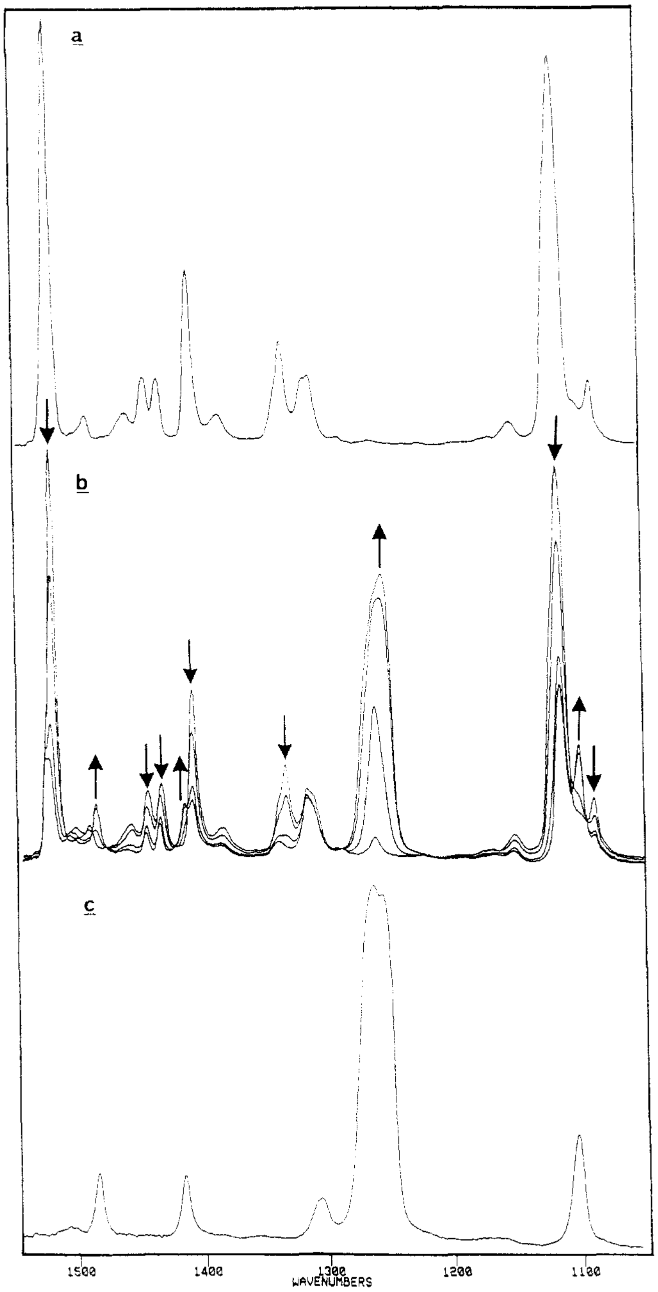


Figure 3. IR spectra recorded from warming a thin film of 1,4-dinitrosobenzene: (a) 160 K, monomer; (b) 170, 173, 174, and 176 K, dimer formation (upward arrows indicate peaks growing and downward arrows indicate peaks decaying upon warming film); (c) 280 K, polymer. All spectra are recorded on the same absorbance scale.

Table II. UV Absorption Spectra of Nitrosobenzenes

compound	λ (nm)
1,4-dinitrosobenzene (Ar)	286, 293 (max), 313, 326, 338, 343, 353, 357
1,4-dinitrosobenzene (film)	302 (max), 320
1,2-dinitrosobenzene (Ar)	261, 266 (max), 284, 331, 343, 359, 379, 388
1,2-dinitrosobenzene (film)	218, 272 (max), 300
nitrosobenzene (Ar)	270, 281 (max), 299, 326, 331, 338

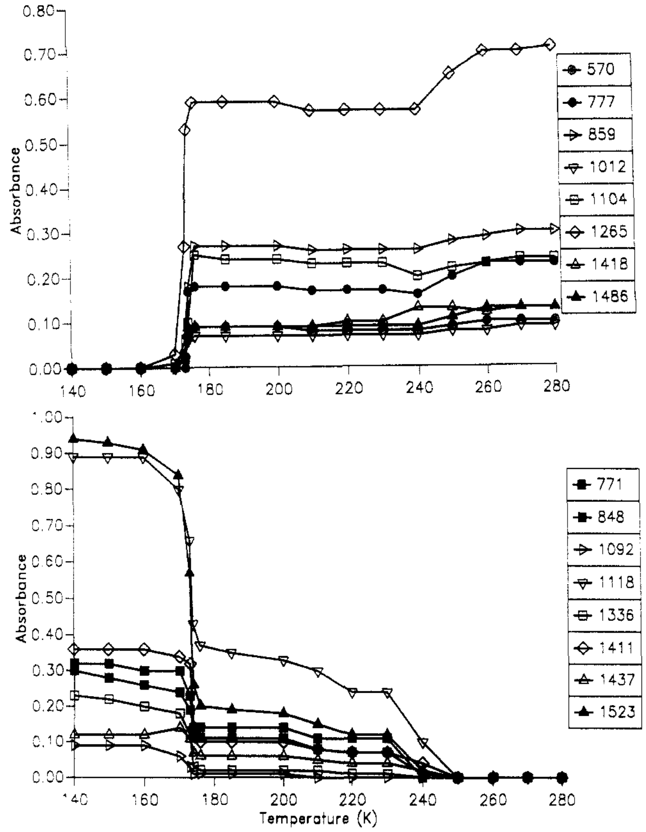


Figure 4. Growth and decay in absorbance of IR bands of polymer and monomer versus temperature.

B. UV Absorption Spectroscopy. Poly(1,4-phenyleneazine *N,N*-dioxide) was deposited with argon onto a sapphire window as described earlier for the IR experiments. The UV absorption spectrum of the sample is shown in Figure 5 along with the spectra for nitrosobenzene and 1,2-dinitrosobenzene. The nitrosoarenes have similar UV absorption spectra (Table II); however, it was not possible to detect the very weak visible bands at ca. 730 nm under our experimental conditions.[1] All three nitrosobenzenes exhibited some vibrational fine structure in their absorption spectra, tailing to the red of the main absorption bands; however, it is more pronounced in the 1,4- and 1,2-dinitrosobenzenes. The UV λ_{max} of the 1,2-isomer is blue-shifted relative to nitrosobenzene, whereas the 1,4-isomer is red-shifted; however, the onset of the absorption spectra of the dinitroso compounds are red-shifted from the onset for nitrosobenzene. This may be due to a lowering in energy of the singlet excited state by charge transfer where both compounds can adopt quinonoid CT structures:

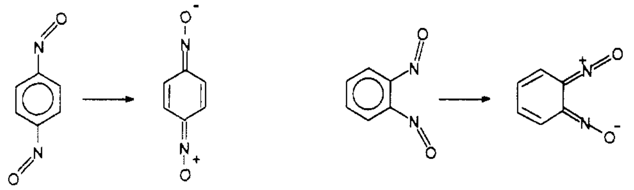


Figure 6 shows the UV absorption spectra recorded from warming a thin film of 1,4-dinitrosobenzene. At 32 K the film has UV absorbances similar to those of the matrix-isolated sample except that there is loss of the red-shifted fine structure. Warming the sample from 32 to 120 K (Figure 6a) results in growth of an absorption at 230–240 nm and a red shift in the onset of the absorption. This may simply be a temperature effect, which has been reported for other molecules; e.g., diazo ketones are blue-shifted when cooled from room temperature to 77 K in hydrocarbon solvents.[12] Further warming from 120 to 180 K causes more of a red shift (Figure 6b) until at ca. 200 K the absorbance at 300 nm decreases rapidly and a peak at 400 nm grows. Further warming from 200 to 290 K results in further decay of the 300-nm peak and the growth of the broad spectrum of the polymer with absorbances at 250 and 400 nm (Figure 6c).

The marked change in the UV absorption spectrum at 180–200 K agrees well with the changes in the IR spectrum

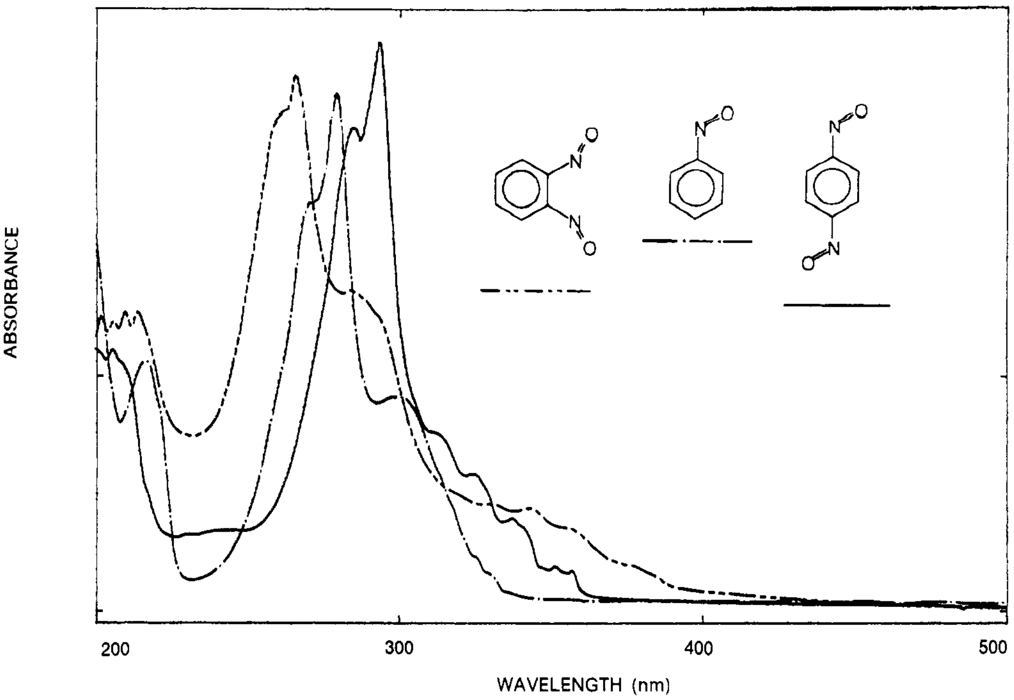


Figure 5. UV absorption spectra recorded in Ar at 14 K: (—) 1,4-dinitrosobenzene; (-·-) nitrosobenzene; (- - -) 1,2-dinitrosobenzene.

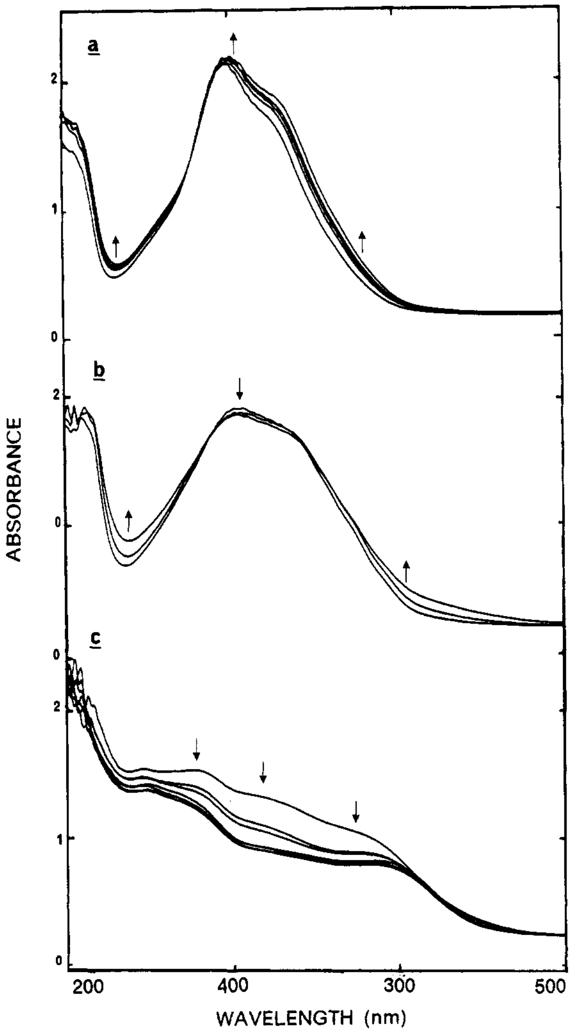


Figure 6. UV absorption spectra recorded from heating a thin film of 1,4-dinitrosobenzene: (a) 32, 60, 80, 100, and 120 K; (b) 140, 160, and 180 K; (c) 200, 220, 240, 260, 270, 280, and 290 K.

recorded at 180 K. In both cases the monomer spectra rapidly change as polymer formation commences. This temperature reflects the low activation energies for dimerization of aromatic *C*-nitroso compounds, which has been reported as 9 ± 2 kcal mol^{-1}.[13] Also the polymer is volatilized at 60–80 °C under vacuum, suggesting a low activation energy for O–N=N–O cleavage. Activation energies of 20 ± 2 kcal mol^{-1} for dissociation of nitrosobenzene dimers and 15 kcal mol^{-1} for tautomerism of benzofuroxans have been reported.[2,14] However, the polymer films are very stable at room temperature and atmosphere pressure due to the higher energy required for cleavage versus dimerization. Thus under relatively mild conditions the polymer is depolymerized and yet also readily polymerizes and consequently is processable with vacuum equipment.[7] However, an interesting feature of the polymerization reaction is the selectivity of the low activation energy process. The IR experiments show no evidence for cis-O–N=N–O formation, yet the matrix-isolated sample indicated that the monomer exists as a 50/50 mixture of rotamers 1 and 2. It might be expected that the rotamers have different selectivities for cis vs trans dimerization. However, the spectrum of the final polymer and the spectra recorded for the growing oligomer show no bands which may be assigned to cis-O–N=N–O stretching. Thus as the monomer reacts, there is rotation to the trans conformation. Also the polymer shows no strong bands at 1530–1570 cm^{-1} for C-NO_2 groups, in contrast to 1,4-dinitrosocyclohexane, which is oligomeric at room temperature with terminal nitro groups.[15] Thus the lack of terminal NO_2 groups and also of residual NO groups in the infrared spectrum indicates that poly(1,4-phenyleneazine *N,N*-dioxide) is a high molecular weight material.

Experimental Section

Poly(1,4-phenyleneazine *N,N*-dioxide) was prepared by a modification of the method described by Khishchenko.[5,7] Liquid Carbonics Ar (99.9995%) was used for the matrix gas. IR spectra were recorded at 1-cm^{-1} resolution for the matrix-isolated sample and at 2-cm^{-1} resolution for the thin films on an IBM Instruments IR44 FTIR spectrometer. UV spectra were recorded at 2-nm resolution on a Hewlett-Packard 8451 diode array UV absorption spectrometer. Samples were deposited onto a CsI window for IR studies and a sapphire window for UV studies. The outer windows of the vacuum shroud were KBr for IR studies and quartz for UV studies. An Air Products CS-202E Displex refrigerator was used to cool the matrix and thin-film samples.

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References and Notes

(1) (a) Gowenlock, B. G.; Luttke, W. *Q. Rev., Chem. Soc.* **1958**, *12*, 321. (b) Coombes, R. G. In *Comprehensive Organic Chemistry*; Sutherland, I. O., Ed.; Pergamon Press: Oxford, 1979; Vol. 2, p 305.

(2) Azoulay, A.; Fischer, E. *J. Chem. Soc., Perkin Trans. 2* **1982**, 637.

(3) Hacker, N. P. *J. Org. Chem.* **1991**, *56*, 5216.

(4) Ruggli, P.; Bartusch, G. *Helv. Chim. Acta* **1944**, *27*, 1371.

(5) Khishchenko, Yu. S.; Makarov, M. A.; Gareev, G. A.; Cherkashina, N. A.; Koptina, G. S. *J. Appl. Chem. USSR (Engl. Transl.)* **1969**, *42*, 2245.

(6) Anderson, L.; Cameron, M.; Gowenlock, B. G.; McEwen, I. J. *J. Chem. Soc., Perkin Trans. 2* **1992**, 243.

(7) Baum, T. H.; Larson, C. E.; Hacker, N. P. *Chem. Mater.*, submitted.

(8) Bradley, G. M.; Strauss, H. L. *J. Phys. Chem.* **1975**, *79*, 1953.

(9) Gowenlock, B. G.; Spedding, H.; Trotman, J.; Whiffen, D. H. *J. Chem. Soc.* **1957**, 3927.

(10) Hatton, W. G.; Hacker, N. P.; Kasai, P. H. *J. Chem. Soc., Chem. Commun.* **1990**, 227.

(11) Gebicki, J.; Kuberski, S.; Kaminski, R. *J. Chem. Soc., Perkin Trans. 2* **1990**, 765.

(12) Hacker, N. P.; Turro, N. J. *Tetrahedron Lett.* **1982**, 1771.

(13) (a) Batt, L.; Gowenlock, B. G. *J. Chem. Soc.* **1960**, 376. (b) Burrell, E. J., Jr. *J. Phys. Chem.* **1962**, *66*, 401. (c) Hoffmann, R.; Gleiter, R.; Mallory, F. B. *J. Am. Chem. Soc.* **1970**, *92*, 1460.

(14) Mallory, F. B.; Mannatt, S. L.; Wood, C. S. *J. Am. Chem. Soc.* **1965**, *87*, 5433.

(15) Childress, W. L.; Donaruma, L. G. *Macromolecules* **1974**, *7*, 427.