

Optical Spectra of Isolated *s-cis*- and *s-trans*-Bithiophene: Torsional Potential in the Ground and Excited States

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Fluorescence excitation and fluorescence spectra of 2,2'-dithienyl (commonly known as bithiophene) seeded into a supersonic helium expansion show complete vibronic resolution. The fluorescence excitation spectrum has two components whose relative intensity depends on expansion conditions. Measurement and analysis of these spectra for systematic variation of expansion conditions leads to their assignment to the *s-trans* and *s-cis* conformers and provides information on the potential for *s-trans* to *s-cis* interconversion in the ground and first excited singlet states.

Introduction

The high-resolution spectroscopic characterization of isolated bithiophene (Figure 1) is of interest for two reasons. First, because it is an oligomer of polythiophene, an understanding of the electronic properties of bithiophene helps us construct models for the more complex polymer. Second, bithiophene is expected to exist in two isomeric forms. A detailed enough spectroscopic characterization could be expected to provide information on the relative energies of these two forms and the barrier to their interconversion in the ground and excited electronic states.

When reduced or oxidized, polymers with extended π -conjugation (for example, polyacetylene or polythiophene) have shown large electrical conductivities.¹⁻³ These polymers have also been shown to have large third-order nonlinear optical susceptibilities. The fact that these interesting and desirable attributes are electronic properties provides much of the motivation for developing a deeper understanding of the electronic structure of these π -conjugated materials. The connection between aspects of the electronic structure such as bond alternation and π -electron delocalization and the interesting properties of these polymers may be derived from the development of a detailed picture of electronic structure of the shorter oligomers and the extrapolation of this picture to the long-chain limit. In the same way that determining the electronic properties of the linear polyenes helps up to understand properties of conjugated polymers such as polyacetylene,⁴ experiments on polythiophene oligomers can help us to understand polythiophene. Of these oligomers, the dimer bithiophene is especially important; it is small enough to be amenable to sophisticated quantum mechanical calculations,⁵⁻¹¹ it can be studied both in the condensed phase and as an isolated molecule in the gas phase, and its π -electron structure is superficially similar to that of octatetraene, which is well understood.

We have reported vibrationally resolved optical spectra of 4.2 K solutions of terthiophene in *n*-decane¹² and bithiophene in *n*-hexane.¹³ To facilitate comparison with quantum mechanical calculations, it is also highly desirable to measure these spectra for the isolated molecules. Further, although theoretical studies have suggested that the ground-state conformation where adjacent rings have a *cis* relationship is only approximately 1 kcal/mol higher in energy than the conformation where adjacent rings are *trans*, only spectra of the *trans* conformer were observed in the condensed-phase experiments. This is because the conditions of the condensed-phase experiments are such that thermodynamic equilibrium is maintained as the temperature is lowered. Since the cooling in a seeded free-jet expansion is much more rapid,

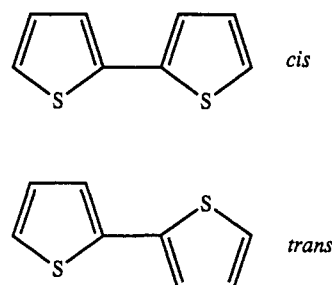


Figure 1. Molecular structures of *cis*- and *trans*-bithiophene.

there is the possibility in these kinds of experiments of freezing in the high-temperature equilibrium and observing the less-stable *cis* conformer. This is in fact the case. In this paper we report the electronic spectra of *s-cis* and *s-trans* bithiophene, extract the enthalpy difference of the two isomers from the observed dependence of their relative abundance on expansion conditions, and compare the observed vibrational fine structure to that expected for various model potentials.

Experimental Section

Bithiophene was purchased from Aldrich Chemical Co. and used without further purification. No contaminants could be detected by either NMR or gas chromatographic analysis. Except for the changes in the sample-handling system that are described below, the free-jet expansion apparatus used was as previously described.¹⁴

The nozzle used in these experiments was a General Valve Iota One System solenoid driven pulsed valve with an 0.8-mm-diameter orifice. Solid bithiophene and helium at a pressure of 1-4 atm were contained in a stainless steel reservoir cylinder (volume ca. 100 cm³) which was heated to 50 °C. The bithiophene seeded helium was conducted from this reservoir to the nozzle assembly through stainless steel tubing jacketed by heating tape. The nozzle was mounted on a translatable 3/4-in. o.d. \times 14-in. long stainless steel tube that extended through the wall of the vacuum chamber. Inside this tube was a heater consisting of a loose spiral of 22-gauge nichrome wire inside a coaxial Pyrex tube (wall thickness ca. 1-mm, o.d. just smaller than the i.d. of the stainless steel tube). The gas temperature just prior to expansion was monitored by a copper constantan thermocouple junction positioned at the entrance (high-pressure side) of the solenoid valve. By changing the current through the nichrome heater the preexpansion temperature of the seeded helium was varied systematically from room temperature to 140 °C. Further variation of the expansion conditions was achieved by changing the distance from the nozzle to the excitation beam.

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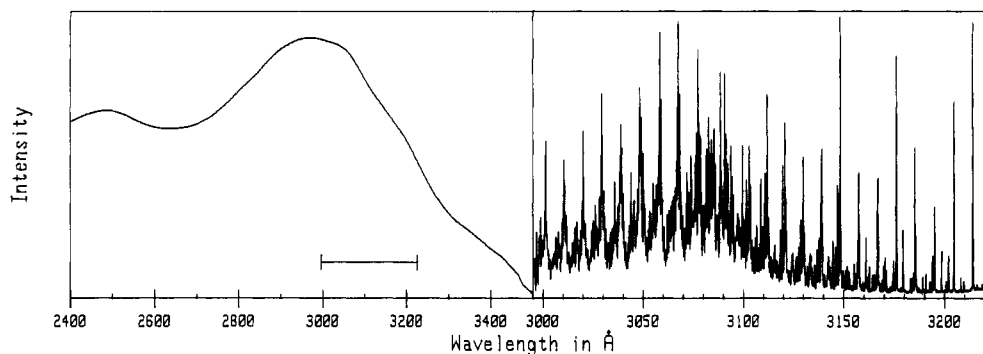


Figure 2. Absorption spectrum of bithiophene vapor at room temperature (left panel) compared to the fluorescence excitation spectrum of bithiophene seeded into a supersonic helium expansion (right panel). The horizontal bar under the vapor absorption spectrum in the left panel shows the wavelength region displayed in the right panel. For the free-jet expansion spectrum the helium pressure in the reservoir was 1.7 atm, the background pressure in the chamber was 10^{-3} Torr, and the intersection of the laser and molecular beams was 12 mm from the 800- μm -diameter nozzle.

Excitation was by a Nd:YAG laser pumped frequency doubled dye laser (Spectra Physics DCR-3D/PDL/WEX) with DCM dye. The laser output was filtered and attenuated so that at the chamber the energy of the ca. 8-ns pulses was ca. $3 \mu\text{J}$. The laser beam and the free jet expansion intersected at a right angle in the center of the vacuum chamber. At the intersection of the molecular and laser beams the laser beam was focused to a 40- μm -diameter beam waist with a confocal length of 3 cm. Light baffles discriminated against scattered light. Fluorescence was collected by an $f/8$ mirror whose optical axis was perpendicular to both the laser and molecular beams, filtered, and detected by a cooled RCA 31034C photomultiplier tube. To measure the spectrum of the emitted light, a $f/8.6$ Jarrell Ash 0.5-m Ebert monochromator with a 1180 groove/mm grating was interposed between the chamber and the photomultiplier.

Results and Discussion

S_1 Optical Spectra and Lifetimes. Figure 2 compares the fluorescence excitation spectrum measured for bithiophene seeded into a supersonic helium expansion to the absorption spectrum measured for the vapor near room temperature. For the free-jet expansion spectrum shown in Figure 2 the helium pressure in the reservoir was 1.7 atm, the background pressure in the chamber was 10^{-3} Torr, and the intersection of the laser and molecular beams was 12 mm from the 800- μm diameter nozzle. The seeded beam fluorescence excitation spectrum that is shown was obtained by collecting all emitted light between 322 and 299 nm. Except for some degradation of the signal-to-noise ratio, the same spectrum is obtained if only the intensity of a single vibronic band is monitored. The origin is at $31\,111 \text{ cm}^{-1}$; our analysis of this spectrum is summarized in Table 1. As will be made clear below, the dramatic increase in information content comes both from the lowering of vibrational and rotational temperature and from freezing out predominantly the *s-trans* conformer from the conformational mixture that is present in the room-temperature vapor.

Except for the 1508-cm^{-1} solvent-to-gas shift, this excitation spectrum is very similar to that measured for bithiophene in *n*-hexane microcrystals.¹³ The relative peak intensities and frequency intervals for the principal vibronic features are nearly the same (Table 2 compares the frequency intervals for the strongest vibronic bands seen in the gas and condensed phases). This similarity in vibronic development is consistent with the idea that the molecular conformation of bithiophene in the two experiments is very similar. In the case of the linear polyenes, the solvent shift behavior of the allowed (S_0 to S_2 in this case) transition is well described by the formula $\delta_{\text{gas}} - \delta_{\text{solvent}} = K(n^2 - 1)/(n^2 + 2)$ where K is approximately $10\,000 \text{ cm}^{-1}$ and n is the solvent refractive index. Using 1.527 for the refractive index of *n*-hexane (footnote 21 of ref 15), the value of K for bithiophene would be 5000 cm^{-1} or approximately half of the linear polyene

value. This is consistent with the smaller peak molar extinction coefficient ($\epsilon = 13\,000 \text{ M}^{-1} \text{ cm}^{-1}$ for bithiophene vs $50\,000 \text{ M}^{-1} \text{ cm}^{-1}$ for octatetraene).

We noticed that the relative intensities of some of the vibronic bands in the fluorescence excitation spectrum of bithiophene seeded into helium free jets depended on expansion conditions. For example, Figure 3 shows how the fluorescence excitation spectrum near the origin changes as the distance from the nozzle to the laser beam is increased. By recording the spectra over a range of expansion conditions, we were able to divide the fluorescence excitation spectrum into two contributions: one whose relative intensity increased with increasing temperature and one that decreased. The component whose relative intensity decreased with increasing temperature is identical to the spectrum shown in Figure 2. The component whose relative intensity increased with increasing temperature is built on an origin at $31\,203 \text{ cm}^{-1}$. We have assigned this new spectrum of *s-cis*-bithiophene and summarize our analysis of bands that can be unambiguously attributed to the carrier of this spectrum in Table 3.

We also measured dispersed fluorescence spectra for excitation at the *cis* and *trans* origins: these are shown in Figure 4. While the electronic excitation energies at high-frequency vibronic intervals for the *cis* and *trans* isomers are very similar, the low-frequency vibronic development is qualitatively different: this is more clearly seen in Figure 5. Because these spectra were measured for excitation at the electronic origin, we know that the observed transitions map the vibrational structure of the ground state. We believe that the low-frequency vibronic structure derives from transitions from the zero-point level in the excited state to hindered rotor levels associated with the interring torsional potential on the ground state. While a definitive assignment of these lines is not realistic given our limited signal-to-noise ratio, it is clear that the spacing of the low lying ground state hindered rotor levels is $40 \pm 2 \text{ cm}^{-1}$ for *cis*-bithiophene. The prominent vibronic lines in the spectrum of the *trans* isomer all show a satellite shifted by $26 \pm 6 \text{ cm}^{-1}$. We believe that this low-frequency mode is associated with inter-ring torsion. The fact that the vibronic developments of the fluorescence spectra measured for excitation at the two fluorescence excitation origins are so strikingly different is persuasive evidence that the origin that grows in as the cooling is less complete is not merely a hot band in the spectrum of the *s-trans* isomer. Because of signal-to-noise limitations and interference from the fluorescence excitation spectrum of the *s-trans* isomer, only the more intense vibronic components of the fluorescence excitation spectrum of *s-cis*-bithiophene could be tentatively assigned. Wavenumber frequencies and assignments of these bands are summarized in Tables 4 and 5.

Lifetime measurements were attempted but, as was the case of the condensed phase, the temporal profiles of the excitation

TABLE 1: Band Positions and Assignments for the Fluorescence Excitation Spectrum of *trans*-Bithiophene Seeded into a He Supersonic Expansion

peak	$\nu - \nu_0^a$	assignment	$\Delta\nu$	intensity	peak	$\nu - \nu_0^a$	assignment	$\Delta\nu$	intensity
1	0	0	0	vs	42	1175	987 + 152	-1	s
2	118	fundamental	0	m	43	1213	187 × 5 + 278	0	vs
3	152	fundamental	0	m	44	1223	1036 + 187	0	m
4	187	fundamental	0	m	45	1237	2 × 152 + 2 × 187 + 278 + 283	-2	s
5	197	fundamental	0	w	46	1242	fundamental	0	s
6	278	fundamental	-1	vs-w	47	1264	1078 + 187	-1	s
7	283	fundamental	0	s	48	1403	fundamental	0	vs
8	306	2 × 152	0	w	49	1309	187 × 7	0	s
9	341	152 + 187	+2	s-w	50	1313	fundamental	0	vs
10	376	187 × 2	0	vs	51	1331	2 × 665	-2	w
11	389	fundamental	0	m	52	1339	1150 + 187	-2	s
12	469	283 + 187	+1	s-w	53	1351	fundamental	0	s
13	492	152 × 2 + 187	+1	m	54	1398	fundamental	0	s
14	525	187 × 2 + 152	+1	m	55	1414	1109 + 304	-1	m
15	560	187 × 3	+1	s-m	56	1428	1242 + 187	-1	s
16	566	2 × 283	0	m	57	1441	fundamental	0	s
17	582	2 × 152 + 278	-1	m	58	1451	1264 + 187	0	s
18	611	152 × 2 + 187 + 118	+2	m	59	1501	1313 + 187	-1	s
19	620	283 + 152 + 187	+2	m	60	1510	3 × 187 + 665 + 283	+1	s
20	651	187 × 2 + 278	-1	vs	61	1523	2 × 187 + 1150	-1	s
21	665	278 + 388	-1	s	62	1546	1264 + 283	-1	s
22	689	fundamental	0	m	63	1553	1150 + 187 + 118	-2	m
23	712	152 + 187 × 3	-1	m	64	1564	fundamental	0	s
24	743	fundamental	0	vs	65	1578	fundamental	0	vs
25	757	197 + 187 × 3	-1	m	66	1584	1398 + 187	-1	vs
26	803	187 × 2 + 278 + 152	-2	m	67	1616	2 × 187 + 1242	0	vs
27	838	187 × 3 + 278	+1	s	68	1666	1264 + 187 + 118	-1	s
28	852	187 + 278 + 388	0	m	69	1714	1242 + 187 + 283	+2	s
29	891	fundamental	0	m	70	1748			m
30	932	187 × 5	-3	m	71	1762	1150 + 611	+1	m
31	945	278 × 2 + 389	-1	m	72	1775	1578 + 197		m
32	955	2 × 152 + 2 × 187 + 278	-1	m	73	1817	1150 + 665	+2	w
33	987	fundamental	0	m	74	1832			m
34	1024	187 × 4 + 278	-2	vs	75	1886			m
35	1036	fundamental	0	s-w	76	1909	1242 + 665	+2	m
36	1056	fundamental	0	s	77	1979	1578 + 152 + 187	-2	m
37	1078	fundamental	0	m	78	1991			w
38	1085	803 + 283	-1	m	79	2092			w
39	1109	fundamental	0	s	80	2198			w
40	1117	fundamental	-1	vs	81	2298			w
41	1150	fundamental	0	vs					

^a $\nu_0 = 31\,111\text{ cm}^{-1}$.**TABLE 2: Comparison of the Principal Vibronic Intervals in cm^{-1} Seen in the Fluorescence Excitation Spectrum of Bithiophene in 4.2 K *n*-Hexane to Those Seen in the Fluorescence Excitation Spectrum of Bithiophene Seeded into a Supersonic He Expansion**

condensed phase ^a ($\nu - 29\,603$)	isolated molecule ($\nu - 31\,111$)	condensed phase ^a ($\nu - 29\,603$)	isolated molecule ($\nu - 31\,111$)
287 ^b	283 ^b	1075	1078 ^b
385 ^b	388 ^b	1150	1166 ^b
572	566	1265	1264
663	665	1324	1328
692	688	1353	1351
772	745	1447	1451
948	944	1551	1553
978	987	1592 ^b	1578
1047	1036 ^b	1610	1616
1058	1056 ^b	1707	1714

^a From ref 25. ^b Assigned as a fundamental.

and emission pulses were indistinguishable. Given the 8-ns fwhm of the excitation pulses, 1 ns is a conservative estimate for the upper bound to the S_2 lifetime of *trans*-bithiophene.

Discussion of the Optical Spectra. Bithiophene may be viewed as a double molecule; that is, as two thiophene molecules connected by a carbon-carbon single bond. The S_1 origin excitation energies of bithiophene (31 203 cm^{-1} for *cis* and 31 111 cm^{-1} for *trans*, corresponding to absorption wavelengths of 3214 and 3205 Å, respectively) are significantly lower than that of the thiophene (41 680 cm^{-1} , corresponding to absorption wavelength

TABLE 3: Band Positions and Assignments for the Fluorescence Excitation Spectrum of *cis*-Bithiophene Seeded into a He Supersonic Expansion

peak	$\nu - \nu_0^a$	rel int	peak	$\nu - \nu_0^a$	rel int
1	0	1	10	676	0.28
2	152	0.13	11	741	0.36
3	186	0.35	12	778	0.23
4	197	0.16	13	834	0.71
5	213	0.14	14	924	0.59
6	373	0.63	15	944	0.89
7	565	0.55	16	965	0.85
8	652	0.77	17	1022	0.81
9	665	0.33	18	1035	0.44

^a $\nu_0 = 31\,203\text{ cm}^{-1}$.

2399 Å) indicating the kind of strong interaction that is only expected if the two rings interact significantly. While X-ray diffraction studies have shown that in crystals bithiophene is in the *s-trans* form and that the rings are coplanar,¹⁶ recent electron diffraction experiments have determined that in the gas phase the inter-ring torsional angle for the *trans* isomer is 64°. The fact that the conformation is significantly changed by the weak nonbonded van der Waals interactions in the crystal suggests the torsional potential near planar *trans* conformation is very flat. Given this, it is possible that the geometry determined by electron diffraction may represent a dynamical average about the global minimum.

The normal mode frequencies for the isolated *trans* molecule generally agree with those determined in the condensed phase

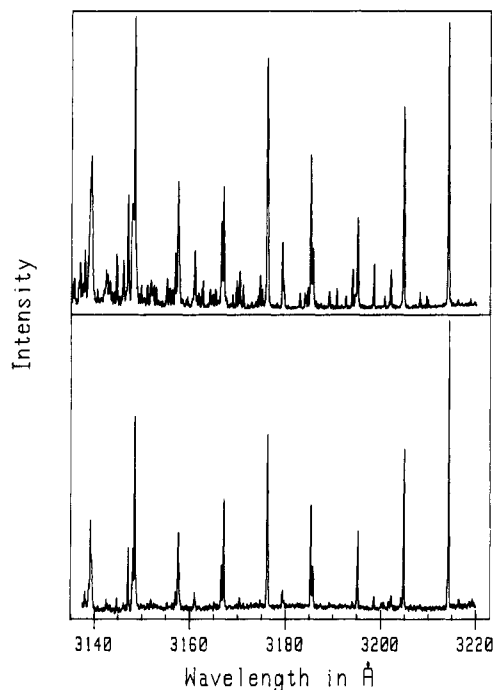


Figure 3. Fluorescence excitation spectra of bithiophene seeded into a supersonic helium expansion at two nozzle distances. The spectrum in the top panel was taken 0.07 mm from the nozzle (top panel); that in the bottom panel was taken 6.4 mm from the nozzle. The expansion conditions for both spectra were the same (reservoir pressure 1.6 atm, preexpansion temperature 93 °C, background chamber pressure 10^{-3} Torr).

experiments. This suggests either that the equilibrium geometry of the *trans* isomer is quite similar in our gas- and condensed-phase experiments or that in each case the torsional potentials near the equilibrium geometry are nearly the same in the ground and excited states. The fact that the excitation energies of the S_1 origins of the *cis* and *trans* isomers differ by only 91 cm^{-1} implies that the inter-ring angle for the *cis* and *trans* isomers are nearly equal. This is consistent with the analysis of the electron diffraction patterns which gave 72° and 64° for the inter-ring angles of the *cis* and *trans* isomers, respectively.

Temperature Dependence. The fact that we can obtain the spectrum of the less-stable *cis* isomer in the free-jet experiments tells us that thermodynamic equilibrium is not maintained as

bithiophene cools. It is then of interest to investigate the dependence of the relative concentration of *cis*-bithiophene on expansion conditions. To estimate the relative contributions of the *cis* and *trans* conformers to a given fluorescence excitation spectrum we fit Gaussians to the origin band profiles measured in that spectrum and compared the Gaussian areas (typical spectra are shown in Figure 3). The *cis*-to-*trans* ratio decreases with increasing distance from the nozzle approaching an asymptotic value at ca. 5 mm downstream (Figure 6). For our conditions the helium translational temperature at 5 mm is approximately 7 K.

To quantitate how the ratio of *cis* origin intensity to *trans* origin intensity is related to the equilibrium established on the high-pressure side of the nozzle, we measured curves such as that shown in Figure 6 for seven different preexpansion temperatures ranging from 58° to 130 °C. Measurements were performed in two ways: (1) by varying the preexpansion temperature and monitoring the spectra at a particular downstream position, then moving further downstream and repeating the variation of preexpansion temperature and (2) by varying the nozzle distance at a given preexpansion temperature, then changing the preexpansion temperature and repeating the variation of downstream distance. Both methods gave the same results. The final data set consisted of 101 data points (14 or 15 nozzle distances for each of the seven preexpansion temperatures) where each data point was the average of at least five independent determinations of the ratio of integrated origin intensities for a specified preexpansion temperature and nozzle distance. In one case where there are 20 repetitions at one temperature and position, *t*-testing at 95% confidence limits gave an error estimate of 8%.

To extract an estimate of the enthalpy difference between *cis*- and *trans*-bithiophene from these data, we extrapolated the data for a given preexpansion temperature to zero nozzle distance by least-squares fitting a straight line to the eight points where the distance from the nozzle was 6 mm or less to get the set of *cis*/*trans* ratio versus temperature values summarized in Table 6. Fitting the data in Table 6 by $R_0 \exp(-\Delta H/kT)$ gives $R_0 \approx 3.7 \pm 0.7$ and $\Delta H = 406 \pm 46 \text{ cm}^{-1}$ ($1.16 \pm 0.13 \text{ kcal/mol}$).

Comparison to Model Potentials. It is informative to compare the spectroscopic results so what would be expected from torsional potentials for bithiophene determined from quantum mechanical calculations. In this we restrict attention to the most recent *ab initio* calculations, those reported by Quattrocchi et al.¹⁰ and those reported by Samdal et al.¹¹ In all of the calculations, *trans*-

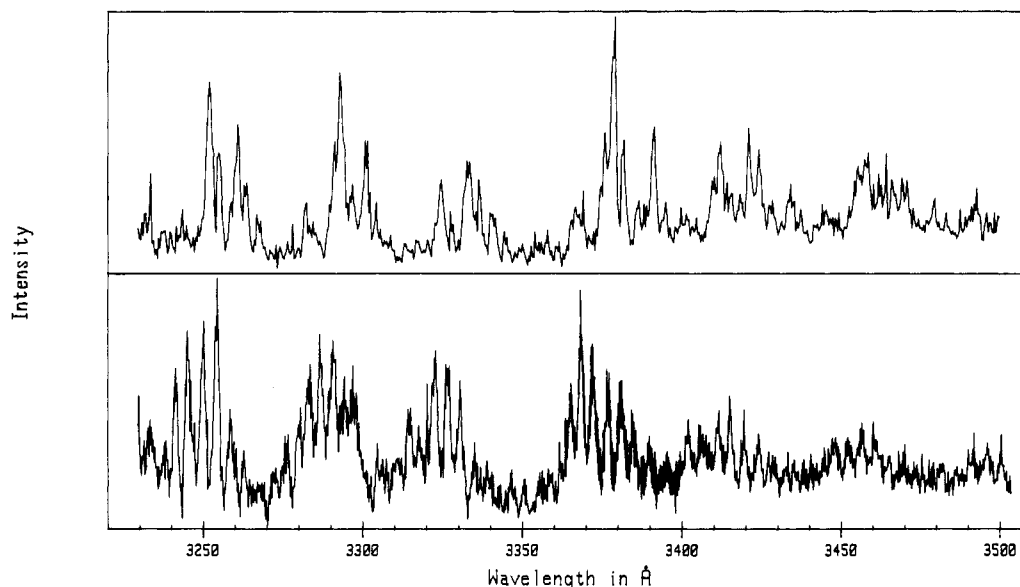


Figure 4. Fluorescence spectra for bithiophene seeded into a supersonic helium expansion. The spectrum in the top panel, obtained by exciting at 31 111 cm^{-1} , is assigned to the *trans* isomer; the spectrum in the bottom panel, obtained by exciting at 31 203 cm^{-1} , is assigned to the *cis* isomer.

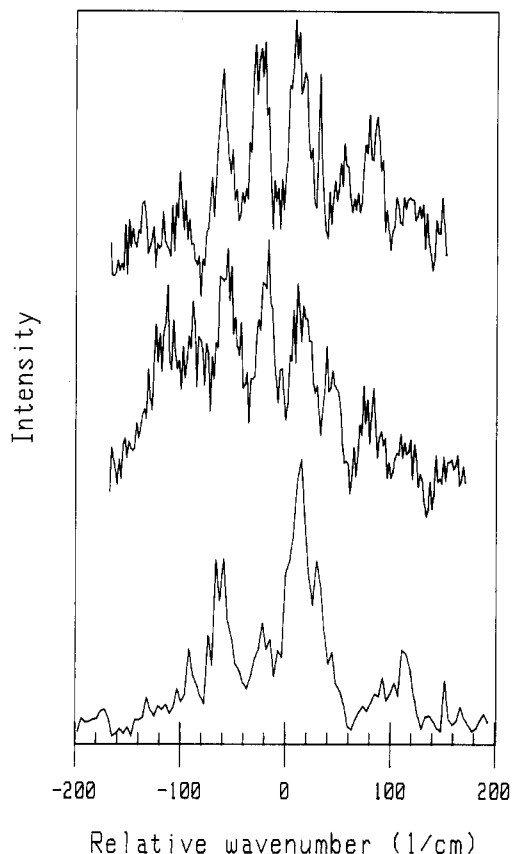


Figure 5. Comparison of the low-frequency vibronic development of the fluorescence spectra of *cis*- and *trans*-bithiophene. The bottom band is from the *trans* isomer spectrum the middle band is from the *cis* isomer spectrum: both ca. 770 cm^{-1} from the origin. The top band is from the *cis* isomer spectrum ca. 1100 cm^{-1} from the origin.

bithiophene is predicted to be more stable than *cis* which agrees with experiment; however, as can be seen in Table 7, the estimates of the relative stability are different for the different calculations. In terms of the stability of the *cis*-bithiophene relative to *trans*-bithiophene, theory and experiment agree within a factor of 2. The RHF/DPZ calculation by Quattrocchi et al.¹⁰ which gave 0.8 kcal/mol is closest to the experimental value. It is interesting that adding sophistication by treating electron correlation with a second-order Møller–Plesset perturbation treatment doubles the discrepancy between experimental and theoretical values. The energy differences obtained in the 3–21G* and 6–31G* calculations of Samdal et al.¹¹ are 0.5 and 0.4 kcal/mol below the experimental value, respectively.

An indication of the extent to which the form of the each of the calculated potentials is supported by the observed spectra can be determined by comparing the energies of the hindered rotor levels computed with these potentials to the low frequency intervals seen in the fluorescence spectra. To make this comparison, we took the coordinate to be the torsional angle between the planes of the two rings which were assumed to rotate as rigid bodies about the inter-ring bond. For bond lengths and angles we used the values determined by X-ray crystallography.¹⁶ The effective moment of inertia as a function of torsional angle, which was calculated numerically, is well represented by the six-term Fourier series summarized in Table 8. Points from the potentials given in refs 10 and 11 read directly from the figures were reasonably fit by the five-term Fourier series also given in Table 8 (the sparseness of the calculated points precluded a more elaborate representation). In each case the matrix of the Hamiltonian consisting of six Fourier terms for the kinetic energy and five Fourier terms for the potential energy was expanded in a basis set of 161 free rotor functions (angular momentum quantum numbers –80 to 80) and diagonalized. Levels were assigned to the *cis* or *trans* isomers on the basis of whether they were localized

TABLE 4: Band Positions, Relative Intensities, and Assignments for the Fluorescence Spectrum of *trans*-Bithiophene Seeded into a Supersonic He Expansion (Excitation Was at 31 111 cm^{-1})

31 111 – ν	frequency	int	$\Delta\nu$
123	fundamental	0.30	0
165	fundamental	0.14	0
218	fundamental	0.18	0
298	fundamental	0.52	0
328	165 \times 2	0.35	–2
381	fundamental	0.39	–2
407	298 + 104	0.25	–5
437	218 \times 2 = 436	0.18	+1
542	218 + 328, 104 + 2 \times 218	0.15	–4
583	fundamental	0.23	0
689	fundamental	0.62	0
716	fundamental	0.31	0
760	fundamental	0.45	–2
785	104 + 298 + 381	0.25	+2
869	381 + 104	0.11	+3
902	fundamental	0.11	
967	fundamental	0.33	0
996	fundamental	0.22	0
1050	fundamental	0.40	0
1076	fundamental	0.34	0
1111	fundamental	0.22	0
1147	165 + 760 + 218	0.18	–4
1197	902 + 298	0.13	–3
1338	fundamental	0.15	0
1268	298 + 967	0.16	–3
1243	fundamental	0.14	0
1300	583 + 716	0.15	–1
1367	fundamental	0.37	–1
1427	fundamental	0.51	0
1455	fundamental	1	0
1480	fundamental	0.58	0
1521	760 \times 2	0.33	–1
1563	fundamental	0.66	0
1594	2 \times 298 + 996, 1300 + 298	0.37	–2
1636	1338 + 298	0.23	0
1650	760 + 3 \times 298, 1480 + 165	0.21	–5
1677	1455 + 218	0.18	–4
1719	fundamental	0.4	0
1743	fundamental	0.53	0
1760	fundamental	0.35	0
1774	1480 + 298	0.29	–4
1794	1455 + 123 + 218	0.29	–2
1818	2 \times 760 + 298	0.67	0
1846	1419 + 123	0.51	–4
1883	1719 + 165	0.27	–1
1931	1338 + 2 \times 98	0.37	–3
1958	1455 + 123 + 218 + 165	0.23	–3
2025	298 + 967 + 760	0.24	0
2109	996 + 1111	0.44	–2
2136	679 + 1455	0.53	–2
2182	1111 + 1076	0.54	–5
2196	298 + 996 + 902	0.43	0
2236	902 + 1338	0.41	–4
2305	967 + 1338	0.3	0

in the *cis* or *trans* wells. In all cases the energy intervals between adjacent levels for the five lowest lying levels of the *cis* isomer were roughly constant with positive anharmonicity (interval decreasing with increasing energy). The characteristic frequency differed significantly from the 40 cm^{-1} seen in the fluorescence spectrum only in the case of the 3–21G* potential of ref 11 which gave 50 cm^{-1} . All of the potential except the 321G//AM1 potential calculated by Quattrocchi et al.¹⁰ gave similar results for the low lying levels of the *trans* isomer: energy intervals 36–40 cm^{-1} with positive anharmonicity. The *trans* levels from the 321G//AM1 potential were distinctly different exhibiting low frequencies (0–1 interval 15 cm^{-1}) and strong negative anharmonicity. While this may be more consistent with the observation of the 26 cm^{-1} satellites in the spectra measured for the *trans* isomer, more definitive conclusions will have to await the results of more elaborate simulations of the spectra. These are currently in progress.

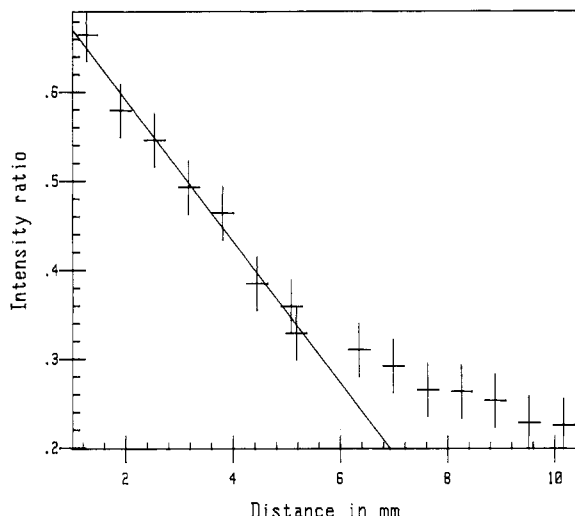


Figure 6. Ratio of the fluorescence excitation origin band intensity of *cis*-bithiophene to that of *trans*-bithiophene as a function of distance from the nozzle. The line is the straight line that best fits the first eight points. For this series the reservoir pressure was 1.7 atm and the preexpansion temperature was 90.3 °C.

TABLE 5: Band Positions, Relative Intensities, and Assignments for the Fluorescence Spectrum of *cis*-Bithiophene Seeded into a Supersonic He Expansion (Excitation Was at 31 203 cm⁻¹)

31 203 - ν	frequency	intensity	$\Delta\nu$
214	fundamental	0.199	0
252	fundamental	0.17	0
268	fundamental	0.18	0
290	fundamental	0.52	0
329	fundamental	0.61	0
378	fundamental	0.598	0
420	fundamental	0.55	0
454	fundamental	0.38	0
514	fundamental	0.24	0
551	fundamental	0.277	0
592	214 + 378	0.32	0
630	252 + 378	0.45	0
667	<i>f</i> , 290 + 378	0.54	0, 1
693	fundamental	0.72	0
711	fundamental	0.67	0
723	454 + 268	0.83	+1
763	<i>f</i> , 514 + 252	0.834	0, -3
793	fundamental	0.79	0
844	630 + 214	0.693	0
881	630 + 252, 667 + 214	0.5	-1, 1
899	630 + 268	0.4	+1
965	711 + 252	0.6	-2
1012	763 + 252	0.56	+3
1059.5	fundamental	0.1	0
1092	fundamental	0.98	0
1164	630 + 2(268)	0.26	+2
1282	763 + 252 + 268	0.27	-1
1339	630 + 252 + 454	0.28	+3
1393	630 + 763	0.4	0
1435	3(268) + 630, 1059 + 378-1	0.48	+2
1463	fundamental	0.74	0
1495	1282 + 214, <i>f</i>	0.7	+1, 0
1530	2 × 763	0.584	
1565	fundamental	0.681	
1604	592 + 793 + 214	0.583	+5
1649	763 + 630 + 252	0.43	+4
1680	1393 + 290	0.44	-3
	1092 + 630	0.456	-3

Conclusions

When bithiophene is seeded into a supersonic expansion, fluorescence excitation and fluorescence spectra that exhibit complete vibronic resolution can be obtained. The fluorescence excitation spectrum has two components whose relative intensity depends on expansion conditions. The spectrum whose relative

TABLE 6: Bithiophene *cis/trans* Ratio Extrapolated to Zero Nozzle Distance versus Preexpansion Temperature^a

temp (°C)	<i>cis/trans</i> ratio	temp (°C)	<i>cis/trans</i> ratio
130	0.90	67	0.70
100	0.77	63	0.68
90	0.74	58	0.64
79	0.68		

^a These data are well fit by $R_0 \exp(-\Delta H/kT)$ where $R_0 = 3.7 \pm 0.7$ and $\Delta H/hc = 406 \pm 46 \text{ cm}^{-1}$.

TABLE 7: Theoretical and Experimental Estimates of the Energy Difference between *cis*- and *trans*-Bithiophene

method	estimate of $E(\text{cis}) - E(\text{trans})$ (kcal/mol)
experiment (analysis of temperature dependence of <i>cis:trans</i> ratios)	1.16 ± 0.13
theory (321-G//AM1 calculations, ref 10)	1.9
theory (RHF/DPZ calculation, ref 10)	0.8
theory (RHF/DPZ calculation plus electron correlation, ref 10)	0.4
theory ^a (321-G calculation, ref 11)	0.6
theory ^a (631-G calculation, ref 11)	0.7

^a Read from Figure 5.

TABLE 8: Fourier Coefficients for Hindered Rotor Kinetic and Potential Energy Terms

<i>n</i>	coefficient of $\cos(n\theta)$				
	inverse inertia (amu ⁻¹ Å ⁻²)	321G//AM1 ^a (cm ⁻¹)	RHF/DPZ ^b (cm ⁻¹)	321G ^{*c} (cm ⁻¹)	6-31G ^{*c} (cm ⁻¹)
0	0.020 607	643	313	296	315
1	-0.000 327	359	186	234	210
2	0.000 169	-345	-115	-2	-94
3	-0.000 96	89	59	141	60
4	0.000 018	155	183	216	166
5	-0.000 003				

^a From Figure 2 of ref 10. ^b From Figure 1 of ref 10. ^c From Figure 4 of ref 11.

weight increases with decreasing temperature is assigned to *s-trans*-bithiophene, the other spectrum is assigned to *s-cis*-bithiophene. By measurement of how the relative weights of the two spectra depend on reservoir temperature the enthalpy difference between the *cis* and *trans* conformations was determined to be $1.16 \pm 0.13 \text{ kcal/mol}$. Comparison with the predictions of recent *ab initio* calculations suggest that the RHF/DPZ potential calculated by Quattrocchi et al.¹⁰ is most in harmony with the experimental results. A more informative analysis of the hindered rotor potential for bithiophene depends on simulations of the spectra that are now in progress.

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