bond couplings between P and the quadrupolar ^{27}Al have been used to assign coordination number for Al·(HMPA)$_4^{3+}$.[15b]

The experiments above have provided unprecedented detail about the solvation behavior of lithium cations in HMPA. Competition among the lithium species for the coordinating agent causes organolithium solutions containing lithium salts to behave in a complex manner.

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Registry No. HMPA, 680-31-9; Li, 7439-93-2; Et$_2$PhB$^-$Li$^+$, 65859-87-2; LiBr, 7550-35-8; PhLi, 591-51-5; 2-methylthiofuran, 13129-38-9.

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Backscattered Raman Optical Activity with a CCD Detector

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Despite the fact that vibrational optical activity in typical small chiral molecules in the disordered phase was first observed by using the Raman optical activity (ROA) technique,[1,2] the complementary vibrational circular dichroism (VCD) technique has attracted more attention because VCD instruments are easier to construct and use. Nonetheless, many ROA spectra have been measured and discussed.[3,4] This communication reports a major breakthrough in ROA instrumentation based on the use of a backscattering geometry (in place of the usual 90° arrangement) together with a cooled charge-coupled device (CCD) detector which should render the ROA technique much more widely applicable.

Basic theory shows that the signal-to-noise ratio (SNR) of many ROA bands should be enhanced considerably in backscattering as compared with 90° and forward scattering. Specifically, the bond polarizability theory for the case of a molecule composed entirely of idealized axially symmetric bonds predicts that a given ROA SNR should be achieved 8 times faster in backscattering than in polarized 90° scattering, which has been confirmed experimentally.[5] Another virtue of backscattered ROA is that the artifacts that plague ROA measurements in 90° scattering are greatly reduced. Also, as in depolarized 90° scattering, there is no contribution to backscattered ROA from the isotropic polarizability-optical activity tensor invariant: this simplifies the analysis of the spectra since the isotropic contribution is the hardest to deal with. The backscattering strategy has enabled ROA spectra to be obtained from unfavorable samples such as aqueous solutions of amino acids,[5] which, despite considerable effort, have never previously yielded significant ROA in 90° scattering.

To this already considerable advance we now add another of comparable significance accruing from the use of a cooled CCD detector in place of the intensified diode array usually used in multichannel ROA instruments. The ultimate sensitivity of ROA measurements is determined by the shot noise of the primary Raman photon flux at the detector. It would therefore be best to avoid an intensification stage in the detector because this lowers the quantum efficiency considerably. Unfortunately, intensification is essential with diode arrays because of the high intrinsic noise characteristics of the naked array. However, the cooled CCD detectors, which are finding increasing use for spectrochemical measurements,[6-8] have extremely low noise levels and can be used without intensification. The importance of this for ROA measurements is that the speed of acquisition (for a given SNR) increases in the same proportion as the increase in quantum efficiency.

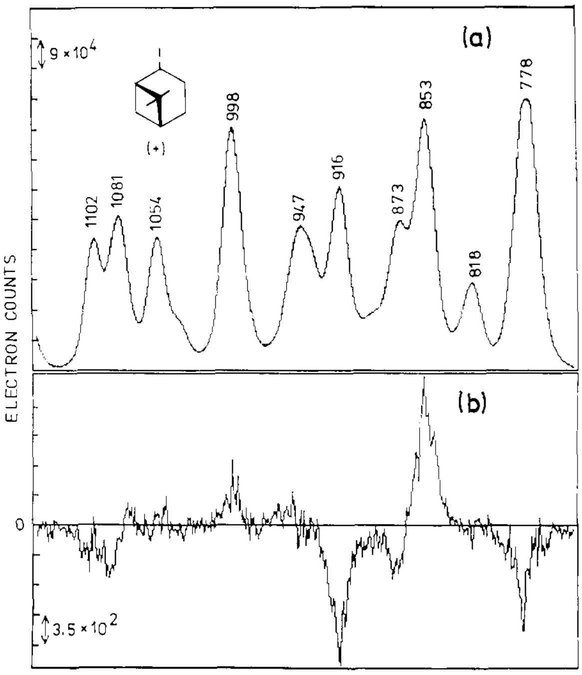

Figure 1. The backscattered Raman spectrum (a) and ROA spectrum (b) of (+)-*trans*-pinane as a neat liquid using a cooled CCD detector. Experimental conditions: laser wavelength 488.0 nm, laser power 600 mW, spectral slit width 6 cm^{-1}, recording time 10 min. The plot is linear in wavelength, but the major band positions are given in wavenumbers (cm^{-1}).

The Glasgow multichannel ROA instrument[9] was used for this study in a backscattering configuration[5] with the intensified diode array detector replaced by a CCD camera. We used the Wright Instruments Model AT1 detector system[10] with the EEV P8603 CCD, which has 385 × 578 pixels, cooled to 200 K with a Peltier cooler. The use of this particular CCD system for the acquisition of conventional Raman spectra has been described previously.[11] The ROA acquisition procedure was similar to that used with the diode array detector:[9] the polarization of the incident laser beam is switched between right and left circular at a suitable frequency in synchronism with the exposure and readout of the detector, the Raman spectrum in left circularly polarized incident light being subtracted from that in right and the difference accumulated. The two-dimensional character of the CCD gives it a great advantage over the diode array for ROA work because the full height of the Raman spectrum can be collected without the need for an optical device such as a cylindrical lens to condense the height of the image to match the height (2.5 mm) of the single pixels in the linear diode array. However, it is essential during readout to bin ver-

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tically down to a single row of data all the signals from the specified area running across the full width of the CCD in order to minimize readout noise.

Figure 1 shows a typical backscattered ROA spectrum obtained with the CCD detector, that of (+)-*trans*-pinane. The quality of this spectrum, acquired in 10 min, appears to be rather better than that acquired in 30 min under similar conditions but using the intensified diode array detector,[5] which indicates an increase in speed by a factor of perhaps 2 or 3. This constitutes an impressive demonstration of the potential value of CCD detectors in ROA work because the alignment and other optical and electronic parameters were far from the optimum since the detector was only available for a few days. Furthermore, the quantum efficiency, and hence the speed, could be increased significantly by using a backthinned CCD for which quantum efficiencies in excess of 80% in the visible can be achieved[7] (the quantum efficiency of the CCD detector used in this study was approximately 15% in the wavelength range of the measured ROA spectrum). Also, the use of one of the larger CCDs of order 1000 × 1000 elements, which are becoming more readily available, together with an appropriate spectrometer, could provide a complete vibrational ROA spectrum covering 50–4000 cm^{-1} in a single exposure.

The results of this study suggest that, by using a backscattering geometry in conjunction with a large backthinned cooled CCD detector, it is now technically feasible to construct an ROA instrument that could be more than 2 orders of magnitude faster than the existing generation of multichannel instruments that utilize the conventional 90° scattering geometry with an intensified diode array detector. Such an instrument could provide a complete high-quality vibrational ROA spectrum of a favorable sample such as a neat liquid in a minute or two. More importantly, it should render a wide range of new samples, including biologically significant molecules in aqueous media, accessible to ROA studies.

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Registry No. (+)-*trans*-Pinane, 4863-59-6.

Parallel Reactivity Sequences in Cycloadditions of Singlet Biradicals and Diels–Alder Reactions. A Common Physical Basis Manifested as Entropy Control or Enthalpy Control[1a]

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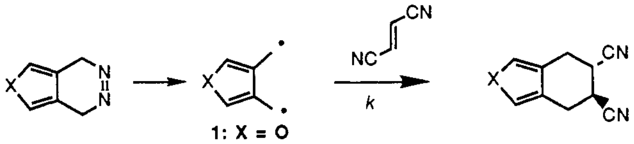
The theoretical rationalizations[2] of the effect of structure on the rates of Diels–Alder reactions and other cycloadditions deal with reactivity sequences that seem to be largely activation enthalpy controlled. For example, the relative reactivities of a series of dienophiles with cyclopentadiene and with 9,10-dimethylanthracene follow $\Delta\Delta H^{\ddagger}$, not $-T\Delta\Delta S^{\ddagger}$. In fact, $\Delta S^{\ddagger}$, is nearly invariant in both of these series, having the value -36 ± 2 cal K^{-1} mol^{-1} for the dienophiles maleic anhydride, fumaronitrile, dimethyl fumarate, and acrylonitrile, the extremes of the range contributing only about 1 kcal/mol (as $-T\Delta\Delta S^{\ddagger}$) to $\Delta\Delta G^{\ddagger}$. The major cause of the >5000-fold range of reactivities of this group of dienophiles is the variation of about 5–6 kcal/mol in $\Delta H^{\ddagger}$.[3]

Table I. Absolute Rate Constants of Reactions of 3,4-Dimethylenefuran **1** and 3,4-Dimethylenethiophene **2** with Alkenes[a,b]

	with **1**[c]		with **2**[d]	
quencher	$k \times 10^{-5}$ M s	temp, °C	$k \times 10^{-5}$ M s	temp, °C
acrylonitrile	3.5	+10		
acrylonitrile	3.7	−10	0.24	−5
acrylonitrile	1.9	−45		
acrylonitrile	1.2	−85		
dimethyl fumarate	440	−10	38	−6
dimethyl fumarate	650	−85	40	−85
fumaronitrile	2200	−10	26	−40
fumaronitrile	2000	−85	46	+20
maleic anhydride	8400	−10	7300	−10
maleic anhydride	3700	−85	5000	−85

[a] See ref 4 for experimental procedures and references to the nanosecond flash kinetic instrumentation. [b] All measurements were carried out in deoxygenated butyronitrile solvent. In earlier work,[4] we found that the rates were insensitive to solvent, the values in acetonitrile and toluene agreeing to within a factor of 2. [c] Excitation with a 337-nm laser pulse. [d] Excitation with a 355-nm laser pulse, except for the maleic anhydride data, which were derived from 337-nm experiments. The yield of transient per pulse (and hence the signal-to-noise ratio) was substantially greater from the 355-nm irradiations, which fall in a stronger absorption region of the diazene precursors of **1** and **2**.

A strong correlation exists between these relative dienophilic reactivities and the relative diylophilic reactivities of the same alkenes toward the singlet biradicals 3,4-dimethylenefuran **1** and 3,4-dimethylenethiophene **2** (generated from the corresponding diazenes.)[4,5] The orders and magnitudes of the relative rates are



1: X = O
2: X = S

essentially the same, despite the factor of 10^{10} in *absolute* rates favoring the biradical reactions. We now find that, in contrast to the diene reactions, the relative rates of the diyl reactions are under activation *entropy* control and are but little influenced by variations in activation enthalpy. Nevertheless, we suggest that although they express themselves here in entropic guise, the causes of the rate order of the biradical cycloadditions are the same as those of the Diels–Alder reactions.

Table I shows that, for all the alkenes, the rates of the biradical cycloadditions are virtually independent of temperature. The acrylonitrile/**1** data cover four temperatures over a 95 °C range and can be expressed in terms of the Arrhenius parameters E_a = 1.3 kcal/mol and $A = 4 \times 10^6$ s^{-1}. Despite the small (in the case of dimethyl fumarate, apparently even slightly negative) activation energies, the rates themselves span a range of about 2200 and 30000 for **1** and **2**, respectively. The reactivities therefore are largely controlled by the entropies of activation.

Why does the same reactivity order appear in the diene and diyl cycloadditions, even though one series is enthalpy controlled

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