

Vibrational Optical Activity. Circular Differential Raman Scattering from a Series of Chiral Terpenes

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Abstract: The circular differential Raman scattering spectra of ten terpenes related to pinane are reported. These were recorded on a multichannel spectrometer developed specifically for this purpose. Several common features are noted in the spectra of these compounds which may form the basis of an absolute configuration rule for molecules belonging to this series.

Circular differential Raman scattering is a property of all chiral molecules.¹ An optically active molecule will scatter right and left circularly polarized light to a different extent and it has been shown that such a circular intensity differential (CID) should appear on all the allowed vibrational bands in the molecule's Raman spectrum.¹ In a molecule with a single conformation there is a unique relationship between its absolute configuration and the sign of the CID on any one of its Raman bands. The absolute configuration of such a molecule can therefore be determined from the sign of any one of the CIDs in its Raman spectrum. It can be shown,² moreover, that a unique relationship exists between the $3N - 6$ internal coordinates describing the relative positions of the N atoms of a molecule and its CID spectrum. Because a molecule possesses precisely $3N - 6$ normal vibrations it is possible, in principle, to invert the circular differential Raman spectrum of a molecule to give its complete stereochemistry (i.e., its bond lengths and bond angles) as well as its absolute configuration. Of course, one normally does not extract all $3N - 6$ fundamentals from a Raman spectrum of a large molecule; on the other hand, bond lengths and most bond angles are usually known in organic molecules containing the more common linkages and specifying the molecular conformation generally reduces to determining a few crucial angles. Circular differential Raman scattering holds the promise, therefore, of offering direct information on both the absolute configuration and the conformation of a molecule. Neither of these goals has yet been realized except in a very limited way for two reasons: (1) no reliable relationship has yet been formulated connecting the observed CIDs with molecular parameters including, of course, the absolute disposition of its atoms, although a certain measure of progress has been recently reported in this regard;³ (2) in most large molecules the assignment of the observed spectral features to normal vibrations and the form of the latter are uncertain. If simple, reliable correlations between the CID and absolute configurations can be found, then an important advance in absolute configuration assignments would have been made.

Several observations of vibrational optical activity have been reported recently both as circular differential Raman scattering⁴ and as infrared circular dichroism.⁵ We recently reported a CID study⁶ of a series of chiral sulfoxides in which the CIDs were related to the absolute configurations of these molecules. Although useful and, in themselves, interesting, these results represented a very narrow range of structural variables. In this paper we describe our observations on a series of much more complicated molecules, terpenes, related to pinane, in order to test the applicability of the technique at a more practical level. In addition, we describe the development of a multichannel device which is capable of collecting data simultaneously over a 350-cm^{-1} portion of the spectrum. This system is of considerable importance to the acquisition of CID spectra not only because of the saving in time but because the

artifacts which tend to plague these measurements are minimized.

Experimental Section

With the exception of (-)-*cis*-pinane, (-)-*trans*-verbenol, and (+)-*cis*-3-pinen-2-ol, which were provided by SCM Glidden, compounds were obtained from Aldrich Chemical Co. Samples were vacuum distilled before use. After distillation the samples did not fluoresce perceptibly when illuminated with 488-nm argon ion laser light.

CID spectra were recorded as follows. The laser beam, initially plane-polarized perpendicular to the scattering plane, was alternately right and left circularly polarized by means of a Pockels (KD_2PO_4) modulator (Laser-metrics). The Pockels cell quarterwave voltage was provided by a regulated dc power supply switched mechanically with mercury-wetted relays (Claire). Mechanical switching was used in order to alternate at the relatively slow speed (approximately 1.27 Hz) required by the multichannel detector, and the modulator switching was slaved to the latter. The scattered light passed through a Polaroid analyzer set so as to accept only the component polarized parallel to the scattering plane (the depolarized component), then collected by an $f/1$ lens and focused on the slit of a Spex Model 1401 double monochromator. An intensified vidicon tube (PAR OMA) was placed at the output port of the first monochromator. (Ordinary Raman spectra of these compounds were measured with an RCA 31034 tube at the output of the second monochromator using ordinary photon counting.) The digitized output of the vidicon was routed to the multichannel analyzer section of the OMA which was modified to allow up or down counting according to the state of an externally imposed logical signal which reflected the state of polarization of the laser beam. Synchronization was accomplished by using the OMA's internal clock pulses which indicate the start of the sweep that interrogates the vidicon image. (Each sweep takes roughly 33 ms to complete.) The spectrum so registered was stored in 500 channels of the multichannel analyzer. Interface electronics were constructed to count a preset number of sweeps (usually 12), after which the sign of the Pockels cell voltage was reversed. In addition, the total number of cycles (one cycle being a pair of consecutive half-cycles in which the sense of circular polarization is opposed) were counted and the data accumulation was stopped when a preset number of cycles was completed (normally 1.4×10^4). Because the vidicon tube has "lag" (i.e., information integrated upon the silicon target is not removed entirely in one sweep), 3 sweeps of the 12 were not kept. This ensured that the information accumulated while the Pockels cell was producing right circularly polarized light, say, did not vitiate appreciably the signal accumulated with left circularly polarized light illuminating the sample.

While the CID spectrum accumulated in one channel (channel A) of the OMA, the sum of the data accumulated during 18 sweeps (nine each with right and left circularly polarized light illuminating the sample) was stored in another memory (memory B). The contents of this memory were then scaled up to reflect the total number of cycles counted and used to calculate the quantity $\Delta = (I^R - I^L)/(I^R + I^L)$. The progress of the data accumulation was monitored on a digital CRT. A hard copy of the data was obtained on paper tape and the Gould plotted peripheral of the IBM system 370 was used to produce the spectra reported below. Three quantities are plotted, $I^R + I^L$, $I^R - I^L$, and Δ . The last quantity consists of short vertical bars whose

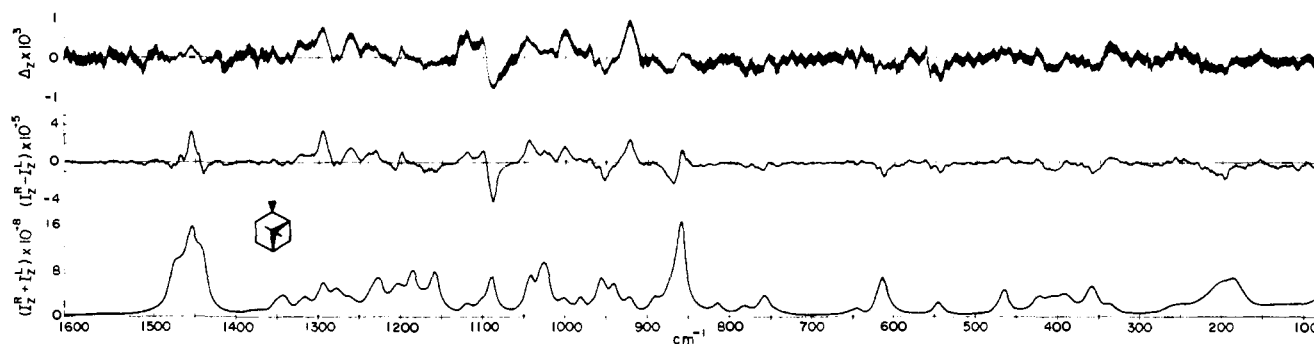


Figure 1. Depolarized Raman (bottom), circular differential Raman (middle), and Δ_z (top) of (*-*)-*cis*-pinane.

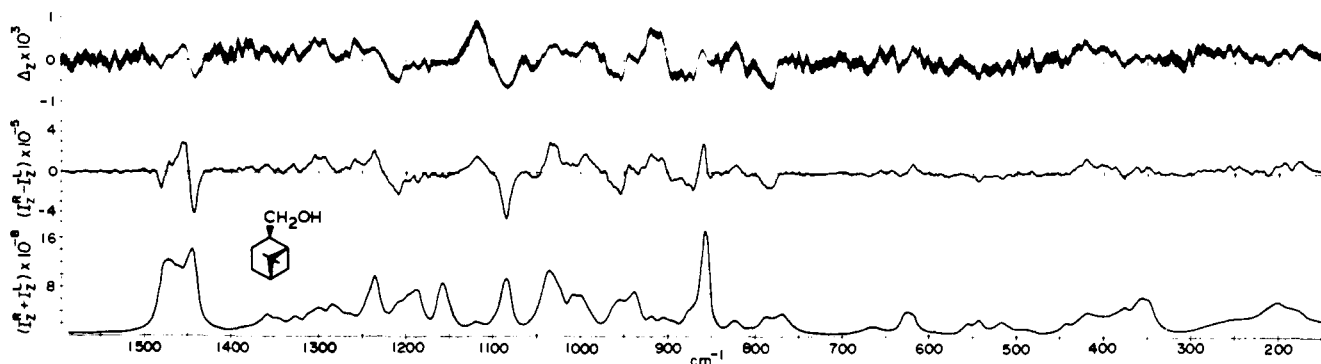


Figure 2. As in Figure 1 but for (*-*)-*cis*-myrtanol.

Table I. The Measured Optical Rotation of the Ten Terpenes

compd	α^{20}_D , deg	remark
<i>cis</i> -pinane	-19.6	neat, 1 dm
<i>cis</i> -myrtanol	-19.0	neat, 1 dm
<i>cis</i> -myrtanylamine	-26.1	neat, 1 dm
α -pinene	+40.2	neat, 1 dm
myrtenol	-44.9	neat, 1 dm
nopol	-34.6	neat, 1 dm
myrtenal	-17.8	neat, 1 dm
<i>trans</i> -verbenol	-134.3 ^a	<i>c</i> 2.5, CHCl ₃
β -pinene	-17.5	neat, 1 dm
<i>cis</i> -3-pinen-2-ol	+97.2 ^a	<i>c</i> 8.4, CH ₂ Cl ₂

^a These values are $[\alpha]^{20}_D$ as opposed to α^{20}_D .

lengths are equal to twice the standard deviation at that frequency. Background counts were subtracted from the sum in calculating Δ except in regions between peaks where some background was retained in order to avoid large, random Δ values in portions of the spectrum devoid of bands. A running average of five adjacent memory locations was taken in order to increase further the signal-to-noise ratio of the CIDs.

A spectral portion approximately 350 cm^{-1} in width was registered by the vidicon at one time with our 1800 groove/mm grating. Although a 100–1500- cm^{-1} spectrum still required approximately 10 h to compile because of the size of the spectral portion counted at one time, the resolution is some fivefold better, and the number of counts effectively gathered per channel roughly tenfold greater than in the conventional, single-channel technique. By using a less densely ruled grating one can trade off resolution for speed and accumulate the entire spectrum in less than 3 h.

Accumulating data originating from several bands at one time not only reduces the time required by the more conventional, single-channel technique to cover a given spectral range but also allows for better suppression of spurious differentials which are most often encountered on highly polarized lines since, at least in some parts of the spectrum, a number of lines of varying degrees of polarization are sampled simultaneously. The reduced counting time also diminishes the influence of instrumental drift on the measured signal. Spectra

covering the range 100–1500 cm^{-1} were obtained by splicing together several 350- cm^{-1} portions, scaling each according to the laser power used. Laser outputs ranging from 200 mW to 1 W were used according to the scattering cross sections of the bands in the part of the spectrum under scrutiny. The crucial Pockels cell alignment was carried out by passing the laser beam, which had previously traversed the modulator, through a rotatable glan polarizer and adjusting the orientation of the former with micrometer screws, varying its tilt and yaw until the signal registered by a silicon photocell on which the laser beam fell was identical for the left and right circular half-cycles at various polarizer positions. The setting was then tested on a highly polarized band in the spectrum to ensure that excessive spurious signals were not encountered.

Results

The circular differential Raman spectra of the ten terpenes examined are shown in Figures 1–10. Because the C–H stretching region showed negligible CIDs, only the portions of spectra from about 100 to 1700 cm^{-1} are shown except for myrtanylamine, whose CH stretching region is included (Figure 11) to illustrate the above statement. The structure and absolute configuration of each are shown on its spectrum. Absolute configurations were obtained from the work of Ohloff and Klein⁷ and Zweifel and Brown,⁸ and optical purity was verified by Na D-line rotation measurements (Table I).

Of the ten terpenes three are based on *cis*-pinane (*cis*-pinane, *cis*-myrtanol, and *cis*-myrtanylamine) and five on α -pinene (α -pinene, myrtenol, myrtenal, nopol, and *trans*-verbenol). In addition β -pinene and *cis*-3-pinen-2-ol were studied. Of the first eight, all but α -pinene had the configuration shown in Figure 12. α -Pinene was of the opposite hand.

The ten molecules chosen allowed one to note the changes in the RCID spectrum with simple changes in structure. So, for instance, a double bond between carbons 2 and 3 (Figure 12) converts pinane to α -pinene. The series α -pinene, myrtenol, and nopol involves changes in the substituent on carbon 2. The three molecules myrtenol, verbenol, and *cis*-3-pinen-2-ol are isomers.

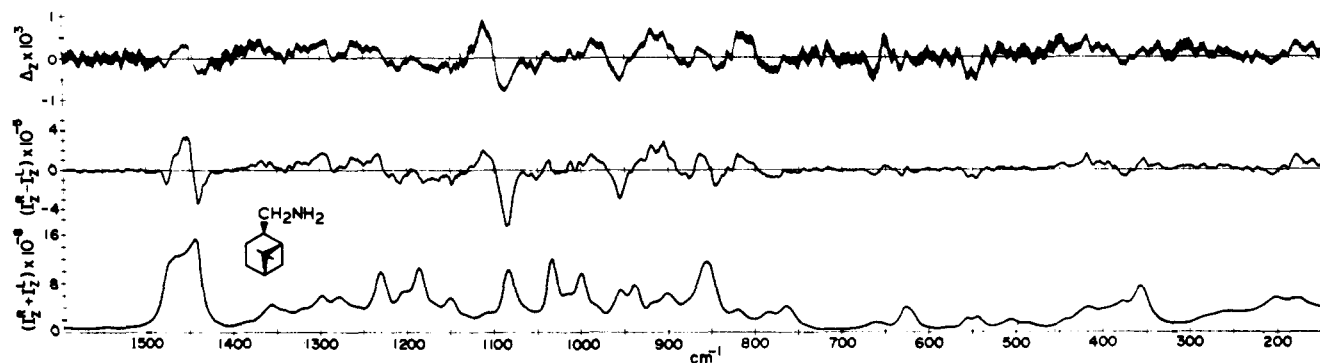


Figure 3. As in Figure 1 but for (-)-*cis*-myrtanylamine.

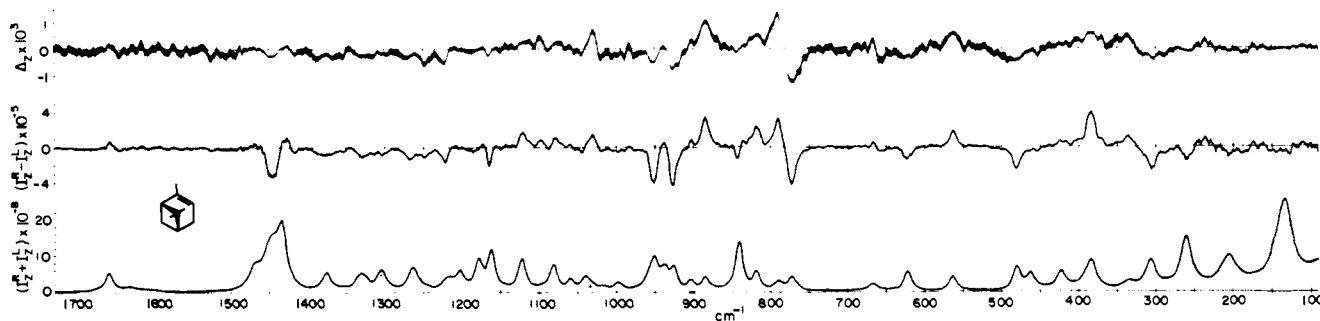


Figure 4. As in Figure 1 but for (+)- α -pinene.

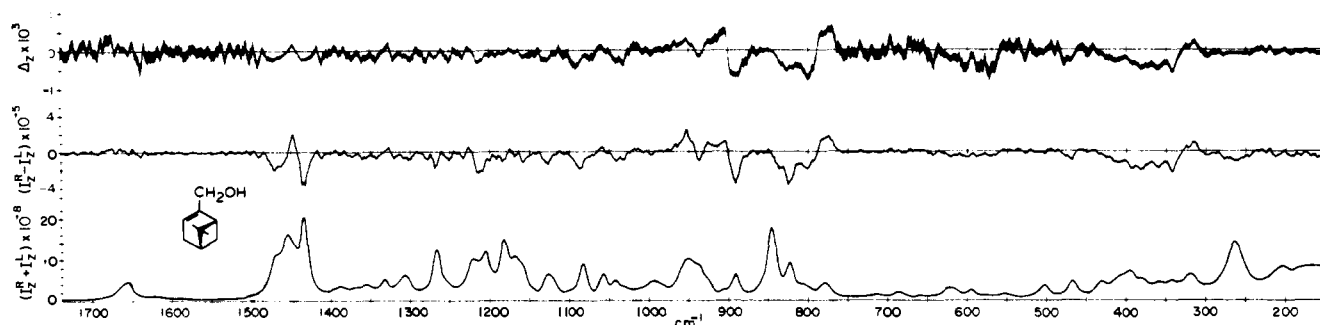


Figure 5. As in Figure 1 but for (-)-myrtenol.

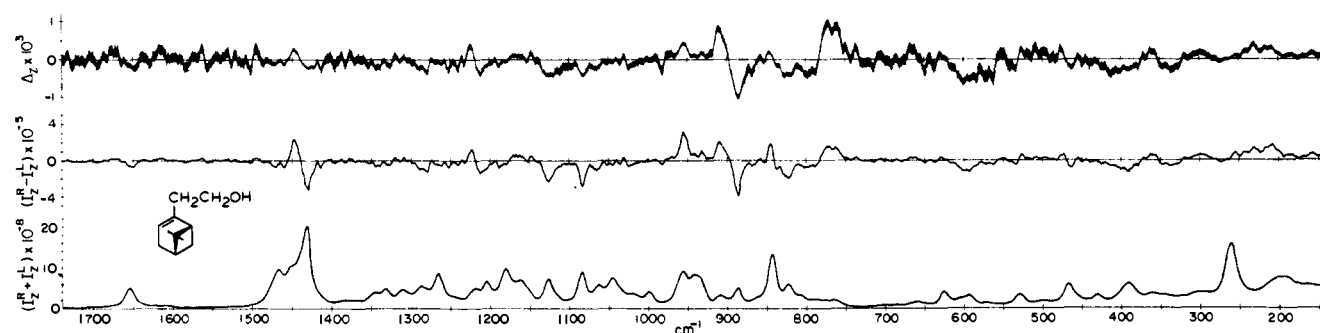


Figure 6. As in Figure 1 but for (-)-nopol.

Broadly, the spectra show strong CIDs in the region associated with carbon skeletal vibrations. In addition, all but verbenol, *cis*-3-pinen-2-ol, and β -pinene show substantial differences in the CH₂ scissoring and CH₃ asymmetric deformation region (1430–1480 cm⁻¹). Although the Δ values associated with these features are small, the strengths of the Raman bands are sufficient to make these features statistically significant. This is gratifying because the CIDs associated with

these vibrations are among the most uniform features in the spectra of the ten compounds studied.

Several similarities and differences between the RCID spectra of the various terpenes are noteworthy. Myrtenol and myrtanylamine, which differ by a trivial substitution, show almost identical RCID spectra. (Their ordinary Raman spectra are also very similar.) Especially noteworthy is the region between 1430 and 1480 cm⁻¹ in these molecules. When the

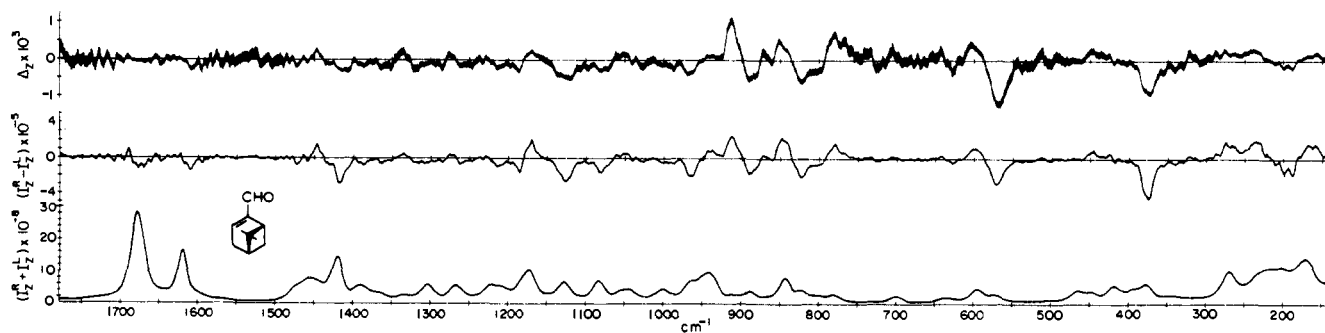


Figure 7. As in Figure 1 but for (-)-myrtenal.

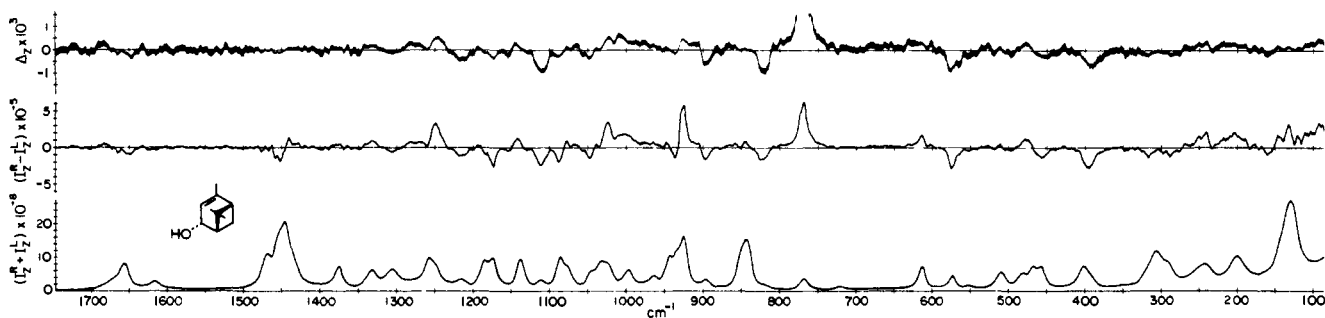


Figure 8. As in Figure 1 but for (-)-*trans*-verbenol.

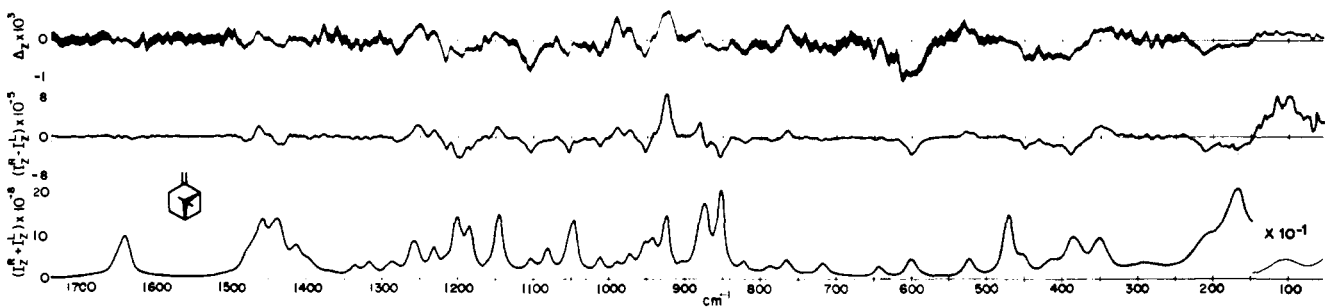


Figure 9. As in Figure 1 but for (-)- β -pinene.

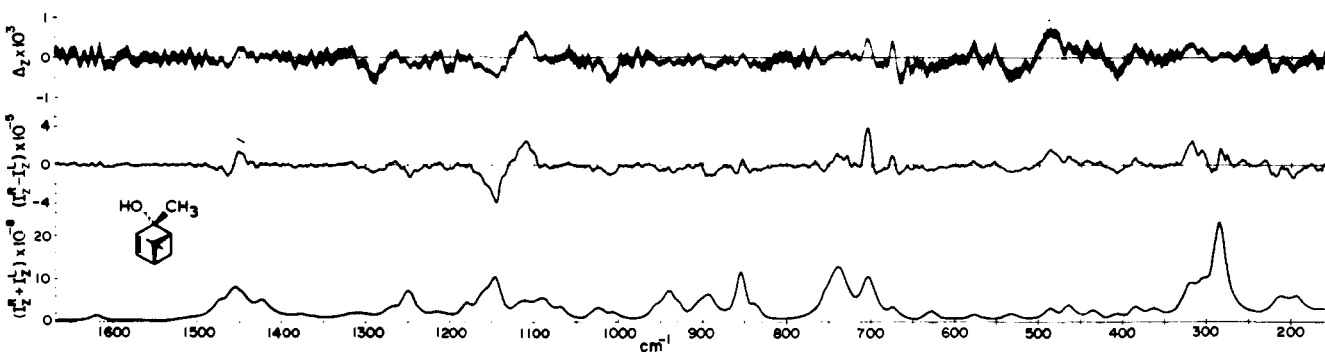


Figure 10. As in Figure 1 but for (+)-*cis*-3-pinen-2-ol.

spectrum of alcohol is shifted by 5 cm^{-1} to lower frequency with respect to that of the amine, one obtains an excellent coincidence in the two RCID spectra, including features which appear only as shoulders. The only CID which differs markedly in the spectra of these two molecules is one at about 1030 cm^{-1} which in the alcohol shows a positive CID while no significant CID is noticeable in that region of the spectrum of the amine.

The CID spectrum of pinane also shows an almost perfect correspondence with those of the previous two compounds

despite a somewhat different aspect to its ordinary Raman spectrum due to small shifts in the positions of bands. The CID spectrum in the CH_2 deformation region of pinane is, however, somewhat reduced from those of myrtenol and myrtanilamine so that the small negative feature at high frequencies is absent. There are also several coincidences in the CID spectra of *cis*-pinane and β -pinene (which also has a saturated cyclohexane ring). For example, the couplet at approximately 920 and 955 cm^{-1} is common to the two compounds as is the negative feature at 600 cm^{-1} (in β -pinene) and 615 cm^{-1} (in pinane). The

Table II. The Sign and Magnitude of the CIDs of the Ten Terpenes on the Raman Lines Indicated

	(-)- <i>cis</i> -pinane	(-)- <i>cis</i> -myrntanol	(-)- <i>cis</i> -myrntan-nylamine	(-)- α -pinene	(-)-myrntanol	(-)-myrntenal	(-)-nopol	(-)- <i>trans</i> -verbenol	(-)- β -pinene	(+)- <i>cis</i> -3-pinen-2-ol
1082	-s	-s	-s	-w	-m	-m	-m	-m	-w	absent ^a
852	+m	+m	+m	+w	0	+w	+w	0	-m	0
822	0	+m	+m	-m	-m	-m	-m	-s	0	absent ^a
656	0	0	0	0	0	0	0	0	0	0
472	0	0	0	0	0	0	0	-w	0	0
387	0	0	0	-s	-w	-s	-w	-w	-w	+w

^a Line absent in Raman spectrum.

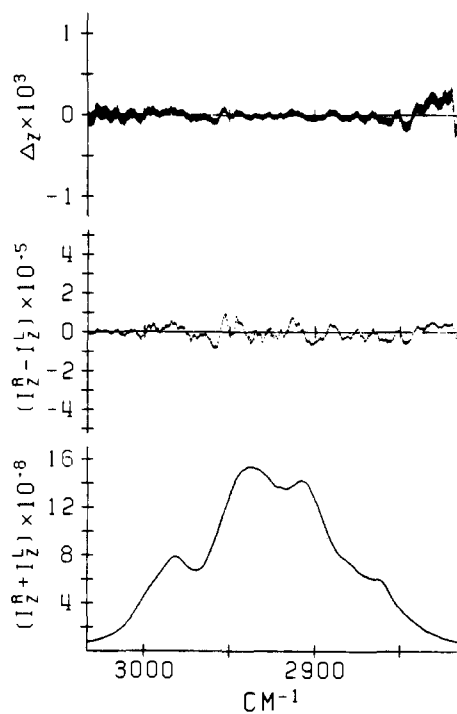


Figure 11. The CH stretching region of the depolarized Raman (bottom), circular differential Raman (middle), and Δ (top) of (-)-*cis*-myrntan-nylamine.

CID features in the CH₂ deformation region of β -pinene are, however, reduced even further than in *cis*-pinane, although the sign order of the lines is maintained.

Among the unsaturated terpenes, nopol and myrntanol have almost identical CID spectra throughout, with very similar CIDs in the CH₂ deformation region. On going from a saturated to the analogous unsaturated molecule, for example, myrntanol and myrntanol, one finds that, while the CH₂ deformation regions are still strikingly similar (although the intensity is somewhat reduced in myrntanol), the rest of the CID spectrum shows few congruent features. To be sure, there are small CIDs which are coincident. The vast majority of strong CIDs, however, do not coincide. Moreover, while the saturated terpene shows strong features from 750 to 1250 cm⁻¹, the range of strong CIDs in the unsaturated terpene is restricted to below 1000 cm⁻¹. Among the five α -pinene derivatives, all but verbenol have quite similar CID spectra apart from small intensity variations. The features in the CID spectrum of α -pinene (in order to maintain uniformity with the majority of the compounds studied, the signed features in the spectrum of α -pinene will refer to (-)- α -pinene rather than the (+) isomer whose spectrum is shown in Figure 1) were, however, more intense than those in the other three, especially the strong positive feature at approximately 925 cm⁻¹ which was almost absent in myrntanol, myrntenal, and nopol. The CID spectrum of verbenol is also very similar to that of (-)- α -pinene except

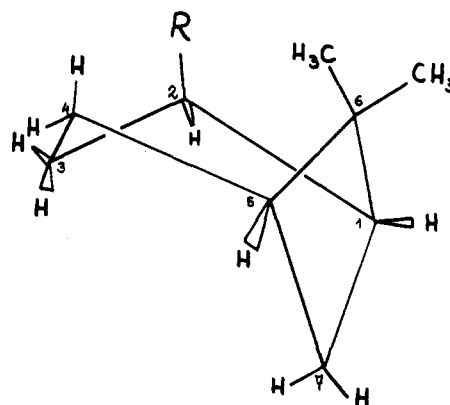


Figure 12. The structures of (-)-*cis*-pinane and related compounds.

for a negative feature at approximately 790 cm⁻¹ and a positive one at 955 cm⁻¹ which are absent in the spectrum of the former. In addition the CH₂ deformation region of verbenol shows almost no Raman optical activity.

Freeman⁹ has reported six unassigned bands which appear to be common in the Raman spectra of many pinane-derived terpenes. These come at 1082, 852, 822, 656, 472, and 387 cm⁻¹. If some or all can be shown to produce consistent CIDs, they could then be used to assign absolute configuration. The results are summarized in Table II.

Discussion

Of the lines which Freeman claims to be common to most of the terpenes we studied, the one at 1082 cm⁻¹ seems the most promising as an index of absolute configuration. This line almost certainly arises from a C-C stretching vibration in the cyclohexane or cyclohexene ring.¹⁰ The feature at 387 cm⁻¹ shows a consistently negative CID in the α -pinene-derived compounds while the line at 822 cm⁻¹ shows negative CIDs for α -pinene derivatives and strong positive CIDs in two of the saturated terpenes.

A detailed discussion of the observed CID spectra is greatly hampered by the fact that unequivocal band assignments are not possible on any of the lines in the spectra, although it is possible to identify with certainty certain classes of vibrations. So, for instance, the bands between 1430 and 1480 cm⁻¹ arise from CH₂ scissoring and CH₃ asymmetric deformations, the bands between 1350 and 1400 cm⁻¹ belong to CH₃ symmetric deformations and to CH₂ wags, and those between 1220 and 1280 cm⁻¹ belong to CH₂ twists. Bands between 750 and 1200 cm⁻¹ arise from C-C stretching, ring breathing, which is a form of C-C stretching, C-C-C bending, and CH rocking. These are usually so thoroughly blended that it is pointless to try to further localize the vibration within the molecule. In rough terms, however, disubstituted cyclohexanes have ring deformation modes between 450 and 500 cm⁻¹, ring "breathing" vibrations between 700 and 800 cm⁻¹, C-C stretching from 1020 to 1090 cm⁻¹, and CH₂ rocking from 1150 to 1200 cm⁻¹.¹⁰ In substituted cyclobutanes the CH₂

rocking normally comes much lower (740 cm^{-1})¹⁰ and the ring breathing much higher, $\sim 1000\text{ cm}^{-1}$. *cis*-Pinane is expected to show a compromise of sorts between characteristic cyclobutane and cyclohexane vibrations.

One set of CID features which might be rationalized is that in the CH_2 scissoring region. All the molecules studied with the exception of (-)-*trans*-verbenol and (+)-*cis*-3-pinan-2-ol have remarkably similar CID spectra in this region, consisting of a positive-negative couplet, with the negative feature at lower wavenumbers. The CIDs were strongest in the saturated terpenes in which a third, weak, negative CID was measured at a higher frequency than the couplet.

Since CH_2 and CH_3 groups are inherently symmetric, the Raman optical activity in this region must arise from coupling among groups which are dissymmetrically disposed. In Figure 12 one sees that the geminal dimethyls are not chirally disposed (at least not locally). Moreover, the methylene group on carbon 3 is not present in the α -pinene derivatives while the CID couplet in the CH_2 region remains. A plausible conclusion might be that the CID couplet originates from coupling between the chirally disposed methylenes situated on carbons 4 and 7. The former is situated on the cyclohexane ring while the latter is on the cyclobutane ring. Thus, although coupling between CH_2 rocking vibrations is expected to be weak, the scissoring frequencies of the two methylenes will be sufficiently similar to allow strong coupling in these modes to give an in-phase and an out-of-phase CH_2 -scissoring vibration. These may be identified by noting the depolarization ratio of the Raman spectrum. In (-)-*cis*-myrtenol, for example, the CID couplet occurs at 1446 cm^{-1} ($\Delta = -0.42$) and 1461 cm^{-1} ($\Delta = +0.33$). The measured depolarization ratios of those two bands are respectively 0.77 and 0.73. The former is, therefore, the out-of-phase motion while the latter is the in-phase scissoring vibration of methylenes 4 and 7.

Barron and Buckingham¹¹ have produced a two-group model for predicting the sign and magnitude of CIDs associated with a chiral dimer, consisting of two achiral monomers, each possessing a unique axis. Although their result is strictly inapplicable in this case, one might expect that at least the correct signs will be predicted by their model. If we take the unique axis to be the bisector of the CH_2 angles in (-)-*cis*-myrtenol, one predicts according to the formulas given by Barron and Buckingham,¹¹ and by making use of a molecular model, that the in-phase, coupled CH_2 deformation will give a positive CID as observed.¹² Moreover, one predicts that the CIDs will decrease in strength on reducing the angle between the projection of the two bisectors on a plane normal to the line joining carbons 4 and 7. On going from myrtenol to myrtenol, carbons 1, 2, 3, 4, and 5 become almost planar¹³ and reference to a molecular model indicates that the angle between the bisectors as defined above does indeed decrease. Substituting on carbon 4 as in *cis*-3-pinen-2-ol and verbenol should cause the CIDs in the CH_2 scissoring region to decrease markedly. This indeed is what is observed. Note also in comparing the CH_2 deformation regions of myrtenol and myrtenal that the strong band in the spectrum of the latter has shifted some 30 cm^{-1} to lower frequencies. The negative CID also shifts and remains about the same strength as in myrtenol. This implies that, while the frequencies of the CH_2 scissoring modes are determined by coupling with other moieties within the molecule in addition to the two ring methylenes considered, the CID arises almost exclusively from the coupling between the methylenes.

The complete RCID spectrum of α -pinene was previously reported by Hug et al.^{4b} and more recently by Barron and Clark.¹⁴ Our spectrum is similar to theirs. Barron and Clark also report the RCID spectrum of β -pinene and several other terpenes including two carenes which are related to α -pinene. They find that the Raman optical activity on the 1082-cm^{-1} line is not a persistent feature in their spectra, although by right

only two of their compounds may be construed to be based on pinane. They propose, moreover, that *gem*-dimethyls in car-3-ene and car-2-ene give rise to significant CID couplets at about 1200 cm^{-1} . All ten terpenes which we have studied possess *gem*-dimethyls and, while nopol and β -pinene do possess couplets in that region, this feature is not a persistent one among the rest of the compounds.

Our results suggest that with multichannel detection Raman optical activity measurements may be made routine. There are encouraging indications, moreover, that absolute configuration and other stereochemical information may be forthcoming from the technique when sufficient systematic measurements are made on series of related compounds.

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- (12) Barron and Buckingham¹¹ give the following formulas for Δ : $\Delta_z^+ = 2\pi R \sin 2\theta / (\lambda(5 + 3 \cos 2\theta))$ and $\Delta_z^- = -2\pi R \cot \theta / (3\lambda)$, where + and - refer to the in-phase and out-of-phase vibrational motions of the two groups, z refers to the CID component of the scattered light polarized parallel to the scattering plane, and R, θ , and λ are respectively the distance between the two groups, the twist angle between the groups measured in a right-hand screw sense, and the wavelength of excitation. Our measured values of $\Delta_z^- = -0.42 \times 10^{-3}$ and $\Delta_z^+ = +0.33 \times 10^{-3}$ are consistent with an angle of 50° and $R = 1.2 \text{ \AA}$ for $\lambda = 488 \text{ nm}$. This gives the correct absolute configuration and a value of θ which is judged to be about correct with the aid of a molecular model. The calculated value of R, however, is about half the actual value. One might claim this to be, then, the first a priori determination of absolute configuration by Raman optical activity.
- (13) B. A. Arbuзов and V. A. Naumov, *Dokl. Akad. Nauk SSSR*, **158**, 376 (1964). The above argument rests on the assumption that pinane is stable in the conformation shown in Figure 12. If carbons 1, 2, 3, 4, 5, and 6 prefer a boat conformation in order to reduce the repulsion between the group R on carbon 2 and the *gem*-dimethyls, then, while the chiral disposition between the methylenes on carbon 4 and 7 remains of the same sense, the angle between their bisectors is reduced and one has an increase rather than a decrease in the value of this angle on going from myrtenol to myrtenol. Under those circumstances the decrease in the couplet on going from the former to the latter compound must be ascribed to another source.
- (14) L. D. Barron and B. P. Clark, *J. Chem. Soc., Perkin Trans. 2*, in press (communicated privately).