

Fourier transform Raman spectroscopy of novel organic systems. The analysis of allenylketenimine-tetracyanoethylene Diels-Alder reaction products

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Abstract—The Diels-Alder reaction products of a series of allenylketenimines with tetracyanoethylene (TCNE) have been studied by Fourier transform (FT) Raman spectroscopy. Several characteristic vibrational features of the adducts are discussed. The application of FT-Raman spectroscopy to the analysis of the adducts is evaluated.

INTRODUCTION

ALLENYLKETENIMINES comprise a novel structural type in organic chemistry, recently synthesized by the reaction of certain titanium metallacycles with tertiary butylisonitrile [1]. Accurate structural data are required on new systems, and are usually provided most readily by ¹³C and ¹H nuclear magnetic resonance (NMR) spectroscopy. However, the allenylketenimines of interest in this work have many adjacent quaternary carbon centres, making unambiguous determination of the structural connectivity difficult. The allenylketenimines also proved to be rather reactive, and somewhat difficult to characterize. Derivatization to produce more stable adducts has previously been used in the characterization of vinylketenimines [2]. The synthesis of the tetracyanoethylene (TCNE) derivatives of the allenylketenimines (see Scheme 1) gave rise to a series of compounds that did indeed prove more stable than the rather labile parent species. This allowed nuclear Overhauser effect (NOE) ¹H NMR techniques to be applied to the adducts, yielding data from which the structure of the parent allenylketenimines could be inferred [3]. Nevertheless, the TCNE adducts still required careful storage to avoid possible degradation (see Experimental section).

Once a structure has been assigned to a chemical system by careful characterization, it often proves necessary to employ a simple and rapid analytical method to subsequent syntheses. Possible reasons for such analyses include establishing the extent of reaction, or the determination of the likely product distribution. Such techniques are available, a technique well-known to organic chemists being infrared (IR) absorption spectroscopy. The basis of success for IR spectroscopy in such applications is the unique nature of the



Scheme 1. Reagents and conditions: i Bu'NC, hexane, 16 h, room temp. (ii) TCNE, CHCl₃, 0°C, 30 min. Note: $Cp = (C_3H_5)^-$ Bu'N = Me₃CN.

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vibrational spectrum obtained from a given system. On examination of a series of closely-related compounds, correlations between spectra are evident that can be ascribed either to common structural features or to specific functional groups [4]. Very often, it is possible to make reasonable assignments of spectral features to vibrational motions on a semi-empirical basis. This is often the only way open to make tenable band assignments, especially where the structures under study are complex. In this paper, we seek to assign the spectra of the allenylketenimine-TCNE adducts in such a manner, identifying the features characteristic of known functional groups, and showing which features are indicative of the underlying cyclic structure. Combining these two data sets should permit the unambiguous assignment of any given adduct.

Infrared absorption spectroscopy proved, at best, partially successful in providing data on the adducts. Although the intense cumulene stretch at around 2000 cm^{-1} disappeared upon reaction with TCNE [1], nitrile stretching bands were either very weak or completely absent. This is curious, although not without precedent [5]. In contrast, nitrile stretching bands are clearly visible in the FT-Raman spectra. In this paper we aim to show that the information obtainable from FT-Raman spectroscopy on the TCNE adducts is extremely useful to the analyst interested in their structure, and indeed complex organic systems in general.

EXPERIMENTAL

The allenylketenimine adducts have the general structure shown in Scheme 1. The functionalities R_1 , R_2 and R_3 are listed in Table 1. The full IUPAC names of this series are somewhat cumbersome for a discussion where frequent comparisons must be made; therefore we adopt the numbering scheme of Ref. [1], which is also indicated in Table 1.

The synthetic details of the allenylketenimine–TCNE adducts are well outlined in Ref. [1]. The Raman spectrometer used in this study is based on the Perkin–Elmer 1720 series FT-Raman prototype. Further details may be found elsewhere [6]. A Spectron model 501 neodymium-doped yttrium aluminium garnet (Nd^{3+} : YAG)-based system lasing at 1064 nm was used to excite the Raman scattering, which was subsequently passed through four Barr Associates rejection filters to suppress the component of the scattered light at the laser wavelength, before falling onto an uncooled indium–gallium–arsenide (InGaAs) photodiode-based detection system. The spectral range covered in this experiment was $300-3300 \text{ cm}^{-1}$, with only Stokes-shifted wavelengths detected. The spectra presented in this paper are the result of 100 accumulated scans of 4 cm⁻¹ resolution, excited with 200–400 mW of laser power. The total scan time per spectrum was approximately 7 min, using a mirror drive speed of 2 mm/s. The Raman spectra have been corrected for wavelength-dependent instrumental response by the method of PETTY *et al.* [7]; the most important outcome is that relative peak heights may be discussed more meaningfully than for uncorrected spectra.

The samples studied were all off-white aggregated solids, kept sealed under refrigeration in the dark when not in use. Given the suspected reactivity of the adducts, long collection times and high laser powers were not used. Although the conditions stated above lead to no sample degradation, and despite the much improved stability of the compounds when compared to the parent species, increases in exposure time or incident power were thought undesirable. Where necessary (2f for example) spectra were collected without removing the solid from the glass sample vial. In situ

Table 1. The nomenclature used in describing the allenylketenimine-TCNE adducts: 1a-f refer to major isomeric form; 2a-f refer to minor

Adduct	\mathbf{R}_1	R ₂	R ₃	Ratio 1:2
a	Ph-	C ₃ H ₇ -	C ₃ H ₇ -	6:1
b	Ph-	Н-	SiMe ₃ -	1:0
с	Ph-	C ₅ H ₁₁ -	SiMe ₃ -	1:0
d	$C_5H_{11}-$	Н–	Ph-	1.4:1
e	$C_{5}H_{11}-$	Ph–	Ph–	3:1
f	C ₃ H ₇	$C_{3}H_{7}-$	$C_{3}H_{7}-$	3:1





Fig. 1. Raman spectrum of 1a. All Raman spectra presented as intensity in arbitrary units against wavenumber shift.

sampling is advantageous where potentially toxic or air-sensitive compounds are under study, and is much easier to implement in Raman spectroscopy than in IR. Excitation in the near-infrared (NIR) at 1064 nm generally avoids severe fluorescence. With reference to sample purity, a rule of thumb for organic systems is that if the sample is "clean" enough to give good, interference-free NMR spectra, then it is more likely to give a good NIR-excited FT-Raman spectrum. Cast alternatively, a recrystallized product will generally give a good spectrum, whereas a columned or chromatographed product generally results in an excellent quality spectrum.

One very important point must be made at this point. The Raman spectra have a simple advantage over the IR spectra; since they were collected directly from the solid phase, no solvent or mulling agent bands complicate the Raman spectra or obscure vibrational detail. This aspect is by no means trivial, although often ignored.

The IR transmission-absorption spectra were recorded in either CCl₄ or CDCl₃ solution using a standard potassium bromide (KBr) window cell on a Perkin-Elmer 1600 series FTIR spectrometer. The spectra presented here are the result of four scans at 4 cm^{-1} resolution. Only two of the 10 spectra are displayed here, between $3500-1000 \,\mathrm{cm}^{-1}$, since the pertinent features of the IR spectra for the whole series can be seen in these two examples, as is explained below.

RESULTS

The Raman spectra of the whole series, 1a to 2f, are given in Figs 1–10. The structural backbone of the series may be described as an essentially-planar, slightly-distorted sixmembered ring; single-crystal X-ray diffraction (XRD) studies on one of the series which crystallized well (1b) revealed the tertiary butylimino-('BuN=) group tilted upwards out of the ring plane, and the R_1 phenyl (Ph-) group twisted at an angle to the plane [8]. These features are primarily due to the steric interactions of the imino group with the trimethylsilyl functional group (Me_3Si_-), and the clash of the Ph- group with the vinylic proton at R_2 . The result is a loss of conjugation, since a wholly-planar compound would have considerably more π -orbital overlap, involving the imino group through to the R₁ Ph- group. The two π -bonds in the ring do, however, remain conjugated. The reason for the existence of two isomers for most of the series is reasonably straightforward to explain. The major isomers (denoted **1a-f** in Table 1) formed in the cycloaddition of the TCNE to the dienophile have the methyl (Me-) group "syn" to the nitrile (CN-) groups; this reflects the approach of the dienophile from the side away from the larger terminal

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group on the parent allene. The structure of the allene is such that the terminal groups lie perpendicular to the plane of the diene, and hence directly on the line of approach of the alkene.

All the spectra are composed of sharp bands superimposed on a flat or gently sloping baseline. 2f constitutes a special case, since it was the only sample which required in situ analysis, whilst also being in very low yield. The background can be partially attributed to fluorescence from the glass container used for this particular sample. In all other cases, good S:N ratios were obtained by co-adding 100 accumulations. A general inspection of the spectra shows that the most intense feature is a sharp band around 1600 cm^{-1} shift in all but one case (1c) and is obviously associated with C=C stretching modes. Phenyl rings usually contribute a band in the $1550-1590 \text{ cm}^{-1}$ region; however, several bands of varying intensity appear in this region, making unambiguous assignment difficult. The next striking feature of the spectra is the sharp, medium-to-weak intensity band around 2250 cm⁻¹ shift, which in some cases displays splitting and/or asymmetry. This band is due to nitrile stretching modes. As mentioned above, the very weak appearance of this mode in the IR absorption spectra provided the initial impetus for this study. Figure 11 shows the IR spectrum of **1a**, which was obtained from CCl₄ solution. The IR spectra of the rest of the series were obtained in CDCl₃ solutions, since this proved to be the solvent of choice for ¹H NMR spectroscopy. With low-yield products, taking both IR and visible-region absorption spectra from previously-prepared NMR solutions is not uncommon practice; the product made up into solution is put to the best possible use, whilst conserving the remaining product for further synthesis. However, in this case the C-D stretching vibration of the solvent appears around 2250 cm⁻¹, obscuring the nitrile region—as is shown in Fig. 12, the IR spectrum of 1b. No such interferences are present in the Raman spectra, as previously noted.

Further inspection of the spectra shows there is always a sharp band close to 1670 cm^{-1} shift, medium-to-weak in intensity. This can be attributed to the C=N stretching mode of the imino group, and is in excellent agreement with previous studies [9, 10]. This provides useful confirmation that the imine is not involved to any great extent in the π -system, since the C=N band shifts to lower frequency on conjugation. The assignment is confirmed by the appearance of an intense sharp absorption band in the IR spectra at almost exactly the same frequency (see Fig. 11).

The other features always present are C-H stretching modes, which occur in two distinct groups. The presence of aliphatic protons is shown by the broad band centred



Fig. 2. Raman spectrum of 2a.



Fig. 3. Raman spectrum of 1b.

around 2930 cm⁻¹, which appears as an asymmetric triplet in several of the adducts. When aromatic C-H is also present, a much narrower band is observed at around $3060-3070 \text{ cm}^{-1}$ shift. If Me₃Si- groups are present, they give rise to another strong C-H stretch at *ca* 2910 cm⁻¹ shift.

Between 1600–1000 cm⁻¹ shift a number of C–H bending and deformation modes occur, which results in a complex pattern of bands, a situation not simplified by the appearance of C–C skeletal stretching modes [11]. However, tentative assignments of certain bands may be made. A weak, slightly broad band appears in all spectra at around 1450 cm⁻¹ shift. This is probably due to the interaction of methyl and methylene (CH₂–) in-plane deformation modes [12]. The band at around 1380 cm⁻¹ shift is probably due to methyl symmetric deformation, although it is unexpectedly absent from the spectrum of 2d. Another sharp band is nearly always present, albeit weakly, at around 1500 cm⁻¹



Fig. 4. Raman spectrum of 1c.



Fig. 5. Raman spectrum of 1d.

shift. This lies outside the usual region for aliphatic methyl or methylene deformation modes. It is most likely to be a phenyl ring-associated band, probably due to a complex ring-stretch plus deformation mode [13]; this assignment is supported by the absence of the band from the spectra of both the **f** isomers, which contain no phenyl groups. The low intensity is probably a reflection that this mode would be Raman-inactive in the more highly-symmetric D_{6h} point group of benzene.

No strong mode indicative of the Si–C can be found in this region. This is not too surprising, since certain stretching modes of alkyl–Si species are strongly IR-active [14]; for instance, Fig. 12 shows the intense Si–C absorption band at 1264 cm^{-1} in 1b. However, the Raman spectra of 1b and 1c do show a pair of bands (at $1304 + 1287 \text{ cm}^{-1}$ shift in 1b and $1299 + 1283 \text{ cm}^{-1}$ shift in 1c) that may well be indicative of the MeSi₃–group. The separation between the peaks is the same in both cases (14 cm^{-1}); both pairs



Fig. 6. Raman spectrum of 2d.



Fig. 7. Raman spectrum of 1e.

are medium to weak in intensity, although each peak is quite sharp; and the higher-shift component is more intense than the lower in both cases. No such peaks are seen in any other member of the series. **1b** may further be differentiated from **1c** simply by the presence of a narrow, medium-intensity band in the former (where $R_2 = H$) at 1331 cm⁻¹ shift and not in the latter ($R_2 = C_2H_7$). Unfortunately, it is not possible to generalize this point to other $R_2 = H$ members of the series, **d** and **f**. One last feature of this region which always occurs no matter whether Ph– groups are present or not is a medium-toweak band at around 1033 cm⁻¹ shift. This sharp band lies within a narrow range of values, from 1039 cm⁻¹ shift in **1f** to 1024 cm⁻¹ shift in **2d**. It is quite conceivable that this band is due to a C–C stretching mode, although it would not be appropriate to go further than stating this band is characteristic of the basic ring and not the variable side groups.

Below 1000 cm⁻¹ shift it is more difficult to draw out characteristic structural features. Information in this region tends to be very specific to a given member of the series, as the



Fig. 8. Raman spectrum of 2e.



Fig. 9. Raman spectrum of 1f.

bands in this area arise from modes prone to couple to other vibrations, reducing their usefulness as group frequencies. There is one very clear exception to this. The presence of aromatic substituents (phenyl rings) is confirmed by the strong and narrow band at approximately 1000 cm^{-1} shift. This is characteristic of the "ring-breathing" phenyl group mode, and serves to identify the group unambiguously [11]. The assignment is quite safe, since both isomers of **f**, which contain no Ph– rings, do not have bands at around 1000 cm^{-1} shift.

A sharp, medium-to-strong intensity band at around 570 cm^{-1} appears in all spectra which probably arises from a mode (or modes) of the tertiary butylimino group carbon skeleton. It falls near the accepted value for an internal quaternary carbon centre [15], although little data seems to be available for this particular vibration. The band itself is both strong in intensity and quite stable in position, falling between 555 cm⁻¹ shift in **2d**



Fig. 10. Raman spectrum of 2f.



Fig. 11. Infrared absorption spectrum of 1a in CCl₄. Solvent bands marked S; bands partially obscured by solvent marked (S). Infrared data presented as % transmission against wavenumber.

and 578 cm⁻¹ shift in **1a**. Thus assignment to the tertiary butylimino group seems reasonable, but is not proven. A similar medium-intensity narrow band occurs around 410 cm⁻¹ shift, between 421 and 391 cm⁻¹ shift; it is quite characteristic of the series, yet is difficult to assign to a specific functional group or structural feature; the same is true of a band at around 630 cm⁻¹ shift which ranges in position between 650–607 cm⁻¹ shift for the high-shift doublet component in **1f** to the low-shift component in **2a**. This particular band is generally weak, can be quite broad, and may be an asymmetric doublet (**1d**) or a single peak (**1a**). The wide spread (± 20 cm⁻¹) from the average position (630 cm⁻¹) might be explained if the normal mode(s) which contribute to this band are sensitive to the exact nature of the substituents.

DISCUSSION

The region between the $1625-1550 \text{ cm}^{-1}$ shift contains bands due to C=C stretching modes, and provides an interesting dilemma concerning their assignment. The strong band at around 1603 cm^{-1} shift (lying between the limits $1615-1594 \text{ cm}^{-1}$ shift) is approximately that expected from a conjugated diene. For instance, the Raman spectrum of liquid 1,3-butadiene exhibites a very strong band at 1637 cm^{-1} shift [11], which is



Fig. 12. Infrared spectrum of 1b in CDCl₃.

due to the two C=C bonds vibrating in-phase. Given the position of the dienyl C=C double bonds in the TCNE adducts, it is not unreasonable to propose that the 30 cm^{-1} downshift is due to mass effects of the groups attached to the dienyl bonds. The problem then arises of how to assign the other bands in the region.

Several complicating factors are plausible. Free dienes may adopt different geometrical conformers, which in principle have different C=C stretching frequencies (due to different vibrational force-fields) and different numbers of Raman-active bands (due to different molecular symmetries). The result is a more complex spectrum, derived from the superposition of the spectra of the individual conformers involved. In favourable cases (such as 1,3-butadiene) the observed spectrum may be interpreted as basically due to only one conformer; this approach works providing one conformer has higher statistical weight than any other. Since the dienyl C=C bonds in the TCNE adducts are part of a six-membered ring structure, the diene is not free to adopt other conformers. However, the spectra of dienes may be complicated by other factors more dependent on the chemical environment of the diene. For instance, the dienyl C=C stretch may be shifted lower in frequency by increased conjugation, whilst fluorinated dienes have higher-shift C=C bands. The number and position of the bands may also change as the number of functional groups appended to the diene increases, or as the nature of these groups is varied.

With these factors in mind, the C=C stretching region of the adducts has remarkably little complication in terms of the number of bands or their positions, given the complexity of the environment in which they exist. The complication is rather more evident in the relative intensity of the bands. Since all adducts except **f** contain phenyl groups, it is safe to assign the band at around 1577 cm^{-1} shift (lying between $1581-1568 \text{ cm}^{-1}$) to the phenyl ring stretching mode, which occurs in benzene at 1596 cm^{-1} [11]. The intensity of this narrow band is quite unpredictable; no consistent explanation for the strength of this band can be reached from the data presented here. A second sharp band of appreciable intensity occurs in the spectra of **1b** (1539 cm^{-1}), **1c** (1536 cm^{-1}), and both isomers of **e** (1556 cm^{-1} major, 1557 cm^{-1} minor). Again, it is difficult to correlate the intensity with any specific feature. Two last points must be made about this region. The first is the splitting of the intense C=C band in **1c** into a doublet at $1601 + 1594 \text{ cm}^{-1}$ shift, which is the only example of such splitting. The second is the very low intensity of the phenyl-associated 1581 cm^{-1} shift band in both isomers of **e**, an adduct with two Ph– groups.

Given the uncertainty in assigning the weaker bands in the area to specific features, and the confusing changes in relative band intensity, it may be that a more formal normal coordinate analysis would at least shed light on the first of these problems. Comparing and contrasting the IR data with the Raman data in the C=C stretching region is also very important for a detailed analysis, since the two techniques are complementary in the sense that IR and Rama spectroscopies have different selection rules. This can be approximated very loosely by the statement that IR spectroscopy is sensitive to change in dipole moment, whereas Raman is sensitive to change in polarizability. Providing the solvent chosen has no interfering absorption bands in the region, there is no reason why IR spectroscopy should not be used to gather data on the C=C bond stretching in these compounds. However, for routine analysis of the TCNE adducts as a whole rather than study on a specific area, FT-Raman proves superior.

The nitrile stretching region around 2250 cm^{-1} shift also provides many interesting points on which to comment. Experimental IR data is available on a wide range of nitrile environments [16–18], and the theoretical basis for the intensity variations and frequency shifts often observed in the IR absorption spectra is well-developed (see, for instance, [19]). Raman data for the intensity of the nitrile species is also available [20]. The broad features of this work can be neatly summarized. Infrared intensities tend to be very unpredictable, and can vary from very intense to almost completely negligible. The intensity can be correlated in certain series to the magnitude of the inductive effect operating, whilst the intensity is reasonably insensitive to the degree of conjugation in the system. It has been proposed that small changes in equilibrium bond length may cause significant change in the equilibrium value of the bond dipole moment, since in general, dipole moment as a function of bond length is a steeply-curved function; this in turn would give rise to a large change in the intensity of absorption. On the other hand, the frequency of the absorption is remarkably stable, depending on the nature of the local electronic structure and hence the chemistry; saturated nitriles absorb around 2250 cm⁻¹, whereas conjugated unsaturated nitriles absorb around 2220 cm⁻¹, with unsaturated unconjugated systems falling in between, along with aromatic systems, where the exact position depends on the nature of the side-groups appended to the cyclic system. Raman spectral data confirm the narrow range for the band position, with a similar trend noted depending on the chemical effects in operation; however, the intensity is more markedly affected by the resonance effect, with conjugated systems being better scatterers than saturated systems to a first approximation. The intensity of the nitrile bands does not vary as widely or unpredictably as does that of the corresponding IR absorption bands. This has been attributed to bond polarizability not being so marked a function of bond length as bond dipole moment over the bond-length region of chemical interest; hence, changes in bond-length are not reflected strongly in the intensity of the scattering. Theoretical study has shown that the frequency is remarkably unaffected by mechanical perturbations, whilst pointing out that it is the CCN-moiety that needs be considered, and not just the CN- in isolation [19]; this is because vibrational calculations show the CN mode mixes significantly with the C-C bond adjacent, but with no others. The authors also show how the IR absorption strengths vary as a strong function of electronic environment.

The vibrational spectra of the TCNE adducts can now be interpreted in terms of these observations. The very low intensity of the nitrile band in the IR spectra has already been mentioned and shown in Fig. 11. The extremely weak absorption of these compounds is clearly a reflection of the unpredictability of the nitrile absorption strength. The simplest model compound is malonitrile $[CH_2(CN)_2]$; JESSON and THOMPSON report and comment on a low value for the molar absorption intensity [16], which leads to the conclusion that dinitriles with CN- groups bonded to the same carbon atom have low IR intensity because of the inductive effect of one CN- group on the other. This is confirmed by the absorption intensity rising as the distance between the two nitrile groups increases, by increasing methylene chain length. If this is the case, then the adducts under study here are good candidates for low absorption intensities, having two more nitrile groups on the β -carbon. This is almost certain to reduce the IR intensity even further, to being almost negligible. (This simple treatment ignores the possibility of Fermi resonance enhancement.) In contrast, a great deal of information can be gained from the Raman spectra, despite the apparent simplicity. In general, there is one sharp band, around 20 cm^{-1} in width, with a definite shoulder or splitting, either to high or low shift. In the single case of the band being split appreciably (1b), the bandwidth of each component is reduced to 10 cm^{-1} . There are two different environments for the dinitrile groups; one has a C=N group on the β -carbon, whilst the other has a C=C. Each has the other dinitrile group as the other β -carbon substituent. It is reasonable, then, to expect a shift or splitting of the CN- band to reflect these two environments. The fact that no major splittings or large shifts are encountered is evidence that the two environments are not widely different in terms of electronic structure. The position of the band ($ca 2250 \pm 5 \text{ cm}^{-1}$) is characteristic of a saturated nitrile group, and is uncorrelated to the nature of the side groups. This confirms the small degree of mechanical coupling between the sidegroups and the CCNbonds. The intensity of the band is, for the most members of the series, medium-to-weak in comparison to the C=C stretch. The intensity does not vary widely, and the band does not become unobservable in any of the series studied. The intensity data thus correlates well to the band-position data, and indicates a saturated nitrile environment.

It would be convenient to be able to distinguish between the major and minor isomers of the adducts by simply looking for a band (or bands) sensitive to the methyl group in the β -position to R₁ being "syn" to the adjacent dinitrile group or not. It is quite plausible that the dinitrile grouping itself would be sensitive, since some steric interaction between the Me- and CN- groups is likely. This might explain the splitting in the nitrile region,

Adduct	Band position(s) (cm ⁻¹)	Description	
 1a	2253 (2248)	Prominent shoulder to low shift	
2a	2247	Reasonably symmetric; bandshape curious	
1b	2265, 2250	Higher-shift band weaker and well-resolved	
lc	2246, ?	Asymmetric (weaker band to high shift)	
1d	2256 (2250)	Prominent shoulder to low shift	
2d	2250, ?	Slight asymmetry on low shift side	
le	2251, ?	Very asymmetric; low shift shoulder	
2e	2253 (2248)	Prominent shoulder to low shift	
lf	2248	Symmetric: curious bandshape	
2f	2249	Symmetric; simple lineshape	

Table 2. Position and bandshape of nitrile stretch

Note: Bandfitting using commercially-available spectral analysis packages could, in principle, yield more accurate estimates for the wavenumber position of the shoulders. However, without guidance on the number of functions to fit, the outcome may be of limited meaning.

since it would affect one dinitrile group and probably not the other. However, the biggest splitting (resulting in well-resolved, separate bands) occurs in **1b**, where it is known that the very bulky Me₃Si– group at R₃ greatly perturbs the imino group. This may result in a "knock-on" effect, either sterically or through conjugation or both, which affects the dinitrile group in the β -position to the imino group; thus the imino-side dinitrile grouping may be affected whilst the other (C=C side) dinitrile group may not. **1c** provides another example of this, with the high asymmetry of the band leading to the conclusion that a second, weaker band is present at higher shift. Thus, isomerism is not necessarily the correct explanation of the nitrile band asymmetry and splitting.

Nevertheless, it is quite plain after examining each pair of isomers that no pair have identical band positions or even the same band-structure in the nitrile stretching region band (see Table 2). Hence, the band may be used to identify between the two isomeric forms of a given adduct unambiguously. This is very good news for analytical purposes, as it completes the picture. Firstly, there are features common to all spectra which permits assignment of the basic allenylketenimine–TCNE structural unit. Secondly, there are sufficient differences to be able to differentiate between individual adducts. Finally, the exact shape of the nitrile band allows unambiguous determination of the isomeric form, once the adduct has been identified. Therefore, it can be stated unambiguously that FT-Raman provides an excellent method for analysis of allenylketenimine–TCNE reaction products.

CONCLUSION

In this work, we have shown that allenylketenimine-TCNE adducts may be differentiated unambiguously by means of NIR-excited FT-Raman spectroscopy, and further how the isomeric form of a given adduct may be deduced. The structural data derived from XRD and NMR studies have been affirmed where possible. The nitrile (CN-) stretch, a band of very low intensity in the IR spectra of the adducts, has been observed in the Raman spectra and discussed.

FT-Raman spectroscopy has been shown once again to be of great value in the characterization of organic species. The good quality of the spectra, the ease of operation of the spectrometer, and the simplicity of sampling make it an attractive additional technique for organic analyses.

Using modern spectrometers, both the FTIR and the FT-Raman spectra can be easily collected and compared. This is most desirable, since the two techniques provide complementary and contrasting information on molecular structure. Such data provide the chemist with a wealth of information, and so the routine collection of both IR and Raman data is to be encouraged.

However, in cases where IR spectroscopy is shown to be inadequate, FT Raman spectroscopy should become a powerful analytical technique in its own right. The characterization of the TCNE-allenylketenimine cycloaddition adducts constitutes one such system where FT-Raman is indeed the method of choice.

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