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The scope and limitations of cyanide groups as direction labels for the conformational analysis of matrix-isolated molecules of low symmetry Part 2: 3-Cyanophenyl azide and two conformationally restrained derivatives

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Abstract

3-Cyanophenyl azide and derivatives with *ortho* methyl groups were photolysed with plane-polarized light in N_2 matrices at 12–20 K. The resulting matrices containing the methyl-substituted derivatives had pronounced IR linear dichroism, which was interpreted in a qualitative way to identify the predominant conformers of the matrix-isolated azides. The cyano groups functioned as *direction labels*, aiding the analysis of the results. Despite problems of band overlap with CN stretches, it was determined, to a high degree of probability, that phenyl azides with one *ortho* substituent exist in N_2 matrices predominantly as the *anti* conformer. In contrast, 3-cyanophenyl azide could not be photo-oriented in N_2 matrices to a significant or reproducible extent, which supports the expectation that the *syn* and *anti* conformers of this azide are virtually equal in energy and thus co-exist in comparable amounts. © 1997 Elsevier Science B.V. All rights reserved.

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1. Introduction

We have been attempting to develop a reasonably straightforward and general method for the conformational analysis of flexible molecules trapped in low temperature matrices. The proposed technique is based on the orientation of trapped molecules by photolysis with plane-polarized light (photoselection) coupled with measurements of IR dichroism [1]. In this context, we have examined the idea of using a rigid linear group, such as CN, to define a particular direction within a molecule of interest. The CN group can thus be regarded as a *direction label*.

The value of such a technique will be greatest, we believe, if the necessary experiments and theo-

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retical treatment of the results are both relatively simple, and, in particular, if valid conclusions about molecular conformations can be drawn from rigorous but qualitative arguments, without the need for computations of transition moment directions. Several theoretical treatments of photo-induced dichroism have been published, and a list of these and a discussion of some applications to matrix-isolated molecules can be found in our earlier paper [1].

We have already set out the qualitative theory for the interpretation of IR linear dichroism induced in matrix-isolated molecules by photoselection, and have shown how the principles can be applied to 2- and 4-cyanophenyl azides [1]. Amongst other things, we were able to conclude, at least with a high degree of probability, that 2-cyanophenyl azide exists in low temperature matrices predominantly as the expected planar *anti* conformer (1) (Scheme 1). In this paper, we examine the related case of the conformations of matrixisolated 3-cyanophenyl azide (2), for which both *syn* and *anti* planar conformers can exist, without it being obvious which, if either, would be energetically preferred.

2. Experimental details

2.1. Equipment

The low temperature cell used in this work, the set-up for irradiation with plane-polarized UV light, and the method employed for recording linearly dichroic IR spectra have all been described previously [1].

2.2. Materials

Research grade N_2 (min. 99.994%) was obtained from B.O.C. Ltd., and was used without further purification. 3-Cyanophenyl azide (2) [2] was prepared from 3-cyanoaniline by the method described by Smith and Boyer for the preparation of 2-nitrophenyl azide [3].

3-Cyano-2-methylphenyl azide (5) (Scheme 3) was prepared in three stages from 2-methyl-3-nitroaniline by diazotization and treatment with CuCN/KCN to give 2-cyano-6-nitrotoluene [4], reduction to 3-cyano-2-methylaniline [5] with Zn/ H₂O/EtOH [6], and finally conversion to the azide by diazotization and treatment with NaN₃, following the procedure described in Ref. [3]. Azide 5 was isolated as an unstable yellow solid, m.p. 106°C (decomp.); ν_{max} (liq. paraffin mull)/cm⁻¹ 2220m (CN), 2150s and 2110s (N₃); $\delta_{\rm H}$ (CDCl₃; Me₄Si)/ ppm 7.35 (3 H, m, aromatic), 2.45 (3 H, s, Me).

3-Cyano-6-methylphenyl azide (6) (Scheme 4) was prepared in three stages from 4-cyanotoluene by nitration to give 4-cyano-2-nitrotoluene [7], reduction with Zn/H₂O/EtOH [6] to give 3-cyano-6-methylaniline [5], and conversion to the azide by the method of Ref. [3]. Azide 5 was isolated as an unstable yellow solid, m.p. 67–68°C; ν_{max} (liq. paraffin mull)/cm⁻¹ 2220m (CN), 2120s (N₃); $\delta_{\rm H}$ (CDCl₃; Me₄Si)/ppm 7.29 (3 H, m, aromatic), 2.28 (3 H, s, Me).

The spectroscopic properties and methods of preparation of azides 5 and 6 established their identities satisfactorily. Both compounds were too unstable at room temperature for elemental analyses to be obtained. All three azides prepared in this work were stored in a freezer for the minimum possible time before being used in the matrix isolation experiments.

2.3. Matrix deposition

The two methyl-substituted cyanophenyl azides (5 and 6) (Schemes 3 and 4) were insufficiently volatile to be made up by standard manometric methods into mixtures with the host gas (N_2) of known concentration. Matrices were therefore deposited by allowing the host gas to pass over the solid azides contained in a glass side-arm attached to the vacuum shroud of the cold cell and condensing the resulting gas mixture on the cold window at 20 K. The flow of gas was controlled by a fine



Scheme 1.



needle valve. With this technique, matrix ratios (host:guest) could not be determined. 3-Cyanophenyl azide was found to be appreciably more volatile, but was deposited in the same way as the other two azides to maintain consistency in the experiments. Once deposited, the matrices were cooled to 12 K before IR spectra were recorded or photolysis carried out. Polarized photolysis was typically carried out until about 50–90% of the deposited starting material had reacted. In a second type of experiment, matrix deposition at 20 K and photolysis were carried out simultaneously, and the resulting matrices were then cooled to 12 K before IR spectra were then cooled to 12 K before IR spectra were then cooled to 12 K before IR spectra were then cooled to 12 K before IR spectra were then cooled to 12 K before IR spectra were then cooled to 12 K before IR spectra were then cooled to 12 K before IR spectra were then cooled to 12 K before IR spectra were then cooled to 12 K before IR spectra were recorded.

3. Results and discussion

3.1. Theoretical principles

The theoretical basis for the qualitative interpretation of IR dichroism arising from photoselection has been discussed previously [1]. Only a brief summary of the main points is given here. Laboratory axes are denoted with upper case letters (X, Y,Z), while molecular axes are denoted with lower case letters (x, y, z).

When photolabile molecules trapped in rigid matrices are photolysed with light travelling in the laboratory Z-direction and plane-polarized in the X-direction, those molecules which have the transition moments of their photo-active electronic transitions aligned with the laboratory X-direction, or close to it, will be photolysed preferentially. After partial photolysis of the sample with plane-polarized light, the residual molecules of the starting material will have a net preferred orientation perpendicular to the laboratory X-direction (photoselection). The electronic absorption corresponding to the photo-active transition will be linearly dichroic: its absorbance with X-polarized light will be less than its absorbance with Y-polarized light $(A_X < A_Y)$. In general, the vibrational absorptions of the oriented sample will also be dichroic. The degree of polarization of an IR band will depend on the angle between its transition moment and the transition moment of the photoactive electronic absorption. If this angle, θ , is 54°, the corresponding IR band will not be dichroic; if $\theta < 54^{\circ}$ then the IR band will be polarized in the same sense as the photo-active transition (A_x < A_{Y}), parallel polarization; and if $\theta > 54^{\circ}$, the IR band will be perpendicularly polarized $(A_x >$ $A_{\rm Y}$). IR bands with θ close to 54° will be only weakly polarized; the degree of polarization of parallel bands will increase as θ approaches zero; while the degree of polarization of perpendicular bands will increase as θ approaches 90°.

By combining photoselection of matrix-isolated molecules with IR dichroism measurements, the vibrational bands of a molecule can be qualitatively divided into three classes: (i) parallel polarized, (ii) perpendicularly polarized and (iii) zero or weakly polarized. This qualitative division can then be used to draw inferences about bond directions within the molecule and hence about molecular structure.

3.2. 3-Cyanophenyl azide (2)

The matrix photolysis of **2** has been investigated previously [8], as part of a study of several 3- and 4-substituted phenyl azides. There are probably two matrix photoproducts: the isomeric didehydroazepines **3** and **4** (Scheme 2). Didehydroazepines such as these have characteristic v(C=C=N) bands near 1900 cm⁻¹, and the samples obtained by photolysis of azide **2** in Ar and N₂ matrices both had two absorptions in this region: 1899 and 1887 cm⁻¹ in Ar, and 1901 and



Scheme 3.



Fig. 1. Polarized azide stretching bands of 5 matrix-isolated in N₂ at 12 K, recorded after deposition at 20 K with simultaneous photolysis with UV light ($\lambda > 220$ nm) polarized in the laboratory X-direction. The X-polarized absorptions are shown with dashed lines, and the Y-polarized absorptions with solid lines. The X- and Y-polarized absorptions for the asymmetric stretch, ν (NNN)_{as}, are virtually superimposed, while the pseudo-symmetric stretch, ν (NNN)_{ps}, is distinctly parallel polarized.

1888 cm⁻¹ in N₂. Results with other 3- and 4-substituted azides, however, showed that the number of IR bands near 1900 cm⁻¹ is not a reliable indicator of the number of didehydroazepine products, and splitting due to matrix site effects or Fermi resonance must be counted as a possibility.

In contrast to our findings with 2- and 4cyanophenyl azides [1] and with the parent compound, PhN₃ [9], matrix photolysis of 2 with plane-polarized light resulted in only very weak and irreproducible dichroism in the IR absorptions of the resulting matrices. This outcome precluded further study of 2, but suggested, though admittedly only with negative evidence, that this azide exists in low temperature matrices as a mixture of the *syn* and *anti* conformers, with neither predominating to a very large degree.

We therefore decided to study two related azides, with built-in conformational restraints in the form of methyl substituents *ortho* to the azido group. An X-ray study of crystalline 4-nitrophenyl azide [10] and Raman studies of liquid PhN₃ [11] have established that phenyl azides exist in planar or near-planar conformations, and a single *ortho* substituent would be expected to favour the *anti* conformation of the azido group, as was found for

2-cyanophenyl azide (1) [1]. On this basis, we expect 3-cyano-2-methylphenyl azide (5) and 3-cyano-6-methylphenyl azide (6) to exist predominantly as the conformers shown, in which the azido group is *anti* to the methyl substituent in both cases, but *anti* to the 3-cyano group in 5 and *syn* in 6 (Scheme 5).

3.3. 3-Cyano-2-methylphenyl azide (5)

The methyl-substituted cyanophenyl azide 5 was isolated in N₂ matrices by passing gaseous N₂ over crystals of the azide and condensing the resulting gas mixture at 20 K. The matrices were then cooled to 12 K and irradiated with plane-polarized UV light ($\lambda > 220$ nm) so as to remove some (typically 50–90%) but not all of the azide. This gave matrices with distinct dichroism in the IR absorptions, but as noted previously [1], higher degrees of polarization could be achieved when the matrices were deposited at 20 K with simultaneous plane-polarized UV irradiation. In either case, IR spectra were recorded with the matrices at 12 K.

Fig. 1 shows light-induced dichroism in the azide stretching bands of 5, and Table 1 lists all the IR bands between 2500 and 400 cm⁻¹ which could be unequivocally assigned to matrix-isolated 5. Because of fears of decomposition of the azide prior to and during matrix deposition, a number of very weak bands, which could not be assigned to 5 with certainty, have been omitted from the data in Table 1.

A major disadvantage of CN groups as direction labels in this type of study, which emerged earlier in our work with 2- and 4-cvanophenvl azides [1], is that the v(CN) frequency is very insensitive to the molecular environment of the CN group. As we have come to expect, the v(CN)absorption of the azide 5 at 2241 cm $^{-1}$ was superimposed upon the corresponding absorption of the photoproduct. It is known that an ortho substituent suppresses ring expansion by migration of the C atom bearing the substituent [12]. and thus we can identify the major photoproduct of 5 as the didehydroazepine 7, which arises by migration of the unsubstituted ortho carbon (Scheme 3). The characteristic ν (C=C=N) absorption of 7 in N_2 matrices was found as a single band at 1909 cm⁻¹.

Table 1

$\bar{\nu}/cm^{-1}$	Dichroism ^a	Assignment ^b	$\bar{\nu}/\mathrm{cm}^{-1}$	Dichroism ^a	Assignment ^b
2241 ^{c,d}	Ţ	v(CN)	1464m		
2126s	0	$v(NNN)_{as}$	1388	1	
1598	0	1 740	1316m		
1585			1294s		v(NNN) _{ns}
1577			793	1	()pa
1474			745	\perp	

Infrared absorptions in the region $2500-400 \text{ cm}^{-1}$, linear dichroism and vibrational assignments for 3-cyano-2-methylphenyl azide (5) photoselected in N₂ matrices at 12-20 K

^a Observed dichroism was either parallel ($\|$), perpendicular (\bot) or zero (0) (see text and Ref. [1]).

^b Notation from Ref. [1].

^c Estimated accuracy of frequencies is $\pm 2 \text{ cm}^{-1}$; bands were weak unless denoted s (strong) or m (medium).

^d Superimposed on product v(CN) band.

Fortunately, the superimposition of the v(CN)bands of 5 and 7 proved less troublesome than similar previous cases. Complete photolysis of matrix-isolated 5 with unpolarized light produced a matrix containing 7 without any preferred orientation. This matrix was then irradiated with planepolarized light, which induced secondary photolysis, as observed with 2-cyanophenyl azide [1]. The residual didehydroazepine photoselected in this way showed pronounced dichroism in the v(C=C=N) and other IR bands belonging to it, but no dichroism in the critical v(CN) band. This fortuitous result implies that secondary photolysis of 7 cannot affect the sign of the dichroism observed for v(CN) in the polarized photolysis of 5. Thus, despite the complete overlap of the v(CN)bands, the direction of polarization of v(CN) for 5 was easily determined as perpendicular (Table 1). It was not possible to estimate the degree of polarization quantitatively, however.

The different polarizations found for the asymmetric and pseudo-symmetric azide stretches of 5 show that the transition moments for these two vibrations are not collinear. There is no reason why



Scheme 4.

they should be, and we have already found that the transition moments for these vibrations do not lie along the NNN axis, deriving a 'best estimate' for their directions of about 30° to the C(1)-N bond [1]. It seems likely that, of the two, the asymmetric stretch would have its transition moment more nearly collinear with the NNN axis, because this vibration is essentially just an oscillation of the central N atom between the other two. Although it is clear that the two azide-stretch transition moments are not collinear, the best estimate for their directions is still 30° to the C-N bond, and we shall continue to use this value for both of them (allowing ample margin for uncertainty) in interpreting the dichroism observed for 5 and 6. We take the direction of the v(CN) transition moment as collinear with the $C \equiv N$ bond.

The observation of parallel polarization in $v(\text{NNN})_{\text{ps}}$ and the in-plane ring mode at 1585 cm⁻¹ and zero polarization in $v(\text{NNN})_{\text{as}}$ and the inplane ring mode at 1598 cm⁻¹ confirms that the electronic transition moment lies in the plane of the molecule, as has been found in the other phenyl azides examined in this way. It is noteworthy that the different polarization behaviour of the azide stretches in 2- and 4-cyanophenyl azides, in 5 and in 6 (see below), shows that the direction of the electronic transition moment does not have a constant angle with respect to the azide group, and therefore varies according the position of the substituents. The observed dichroism of v(CN) and the azide stretches place limits on the possible



Fig. 2. Planar conformations of 5. Estimates of the directions of the transition moments of v(CN) and the azide stretches are shown for each structure. The shaded areas define probable limits for the direction of the transition moment of the photoactive transition as derived from the dichroism of three IR bands: CN the v(CN) band, Az(as) the asymmetric azide stretch, Az(ps) the pseudo-symmetric azide stretch. See text for a discussion.

direction of the transition moment of the photoactive electronic absorption. Allowing margins for uncertainty, these limits are shown diagrammatically for both the *anti* and *syn* conformations of 5 in Fig. 2. In constructing these diagrams, we have assumed the following limits on the angle between the photo-active transition moment and the vibrational transition moments: $0-45^{\circ}$ for distinctly parallel polarized bands, $54 \pm 25^{\circ}$ for zero or very weakly polarized bands, and $60-90^{\circ}$ for clearly perpendicularly polarized bands. The limits consistent with the observed dichroism of the v(CN)band and each of the azide stretches are shown as shaded areas in Fig. 2.

In the diagram for the *anti* conformation of 5, the three shaded areas all overlap, giving a range of directions in which the photo-active transition moment could lie. The centre of this range is shown in Fig. 2 with an arrow labelled PA. The diagram for the *syn* conformation, however, shows good overlap between the shaded areas for v(CN) and $v(NNN)_{ps}$ but virtually zero overlap for v(CN) and $v(NNN)_{as}$. In other words, the observed polarizations for the v(CN) and asymmetric azide stretching bands are inconsistent with the *syn* conformation. Provided the assumption of a planar structure for 5 is correct, the results clearly show that 5 exists in N₂ matrices in the *anti* conformation, as expected.

3.4. 3-Cyano-6-methylphenyl azide (6)

The methyl-substituted cyanoazide 6 was photo-oriented in N_2 matrices at 12–20 K as described for its isomer 5. Fig. 3 shows light-in-



Fig. 3. Polarized azide stretching bands of **6** matrix-isolated in N₂ at 12 K, recorded after deposition at 20 K with simultaneous photolysis with UV light ($\lambda > 220$ nm) polarized in the laboratory X-direction. The X-polarized absorptions are shown with dashed lines, and the Y-polarized absorptions with solid lines. The X- and Y-polarized absorptions for the pseudo-symmetric stretch, ν (NNN)_{ps}, are virtually superimposed, while the asymmetric stretch, ν (NNN)_{as}, is distinctly perpendicularly polarized.

Table 2

$\bar{\nu}/\mathrm{cm}^{-1}$	Dichroism ^a	Assignment ^b	$\bar{\nu}/cm^{-1}$	Dichroism ^a	Assignment ^b
2241 ^{c,d}		v(CN)	1406m	0	
2230		$\nu(CN)$	1385	0	
2134s	Ĩ.	$\nu(NNN)_{as}$	1320	0	
2120 <i>s</i>	\perp	v(NNN) _{as}	1301 <i>s</i>	0	$\nu(NNN)_{ns}$
2086m	\perp	v(NNN) _{as}	1296s	0	$\nu(NNN)_{rs}$
1611	0		1284	0	· · • •
1598			1196	\perp	
1568m	Ö		875	\perp	
1508m			827	\perp	
1488 1450	∥ ⊥		792	\bot	

Infrared absorptions in the region $2500-400 \text{ cm}^{-1}$, linear dichroism and vibrational assignments for 3-cyano-6-methylphenyl azide (6) photoselected in N₂ matrices at 12-20 K

^a Observed dichroism was parallel (\parallel), perpendicular (\perp) or zero (0) (see text and Ref. [1]).

^b Notation from Ref. [1].

^c Estimated accuracy of frequencies is $\pm 2 \text{ cm}^{-1}$; bands were weak unless denoted s (strong) or m (medium).

^d Superimposed on product $\nu(CN)$ band.

duced dichroism in the azide stretching bands of **6**, and Table 2 lists all the IR bands between 2500 and 400 cm⁻¹ which could be unequivocally assigned to matrix isolated **6**. As with the isomer **5**, fears of decomposition of the azide prior to and during matrix deposition have led us to omit from the data in Table 2 a number of very weak bands, which could not be assigned to **6** with certainty.

On photolysis in N₂ matrices, **6** underwent ring expansion to a didehydroazepine, identified as **8**, with a single v(C=C=N) band at 1904 cm⁻¹ (Scheme 4). As expected, the v(CN) bands of **6** and its photoproduct **8** were superimposed, but, as in the case of **5**, the photoproduct v(CN) band developed no dichroism during polarized secondary photolysis, so we could confidently identify the polarization of the v(CN) band of **6** as parallel (Table 2). Clearly, no quantitative estimate could be made of the degree of polarization of this band.



Scheme 5.

That the transition moment of the photo-active absorption lies in the plane of the molecule, as normal, is confirmed by the zero polarization of $v(NNN)_{ps}$ and parallel polarization of v(CN) and the in-plane ring mode at 1598 cm⁻¹. The polarizations of the $\nu(CN)$ and azide stretching bands of 5 and 6 contrast markedly: the v(CN) band is perpendicularly polarized in 5 but parallel polarized in 6; the asymmetric azide stretch is unpolarized in 5 but perpendicularly polarized in 6; and the pseudo-symmetric stretch is parallel polarized in 5 but unpolarized in 6. Thus the expected conformational difference between these two isomers is immediately reflected in the IR dichroism of the CN and azide groups. The CN and azide stretches of 6 are split, probably by Fermi resonance. This splitting of the azide stretches, although not apparent in the IR spectrum of 5, is common for phenyl azides [13].

The observed dichroism can be interpreted, as was demonstrated for 5, by considering the limits which are placed on the direction of the transition moment of the photo-active transition. Fig. 4 gives the results of this analysis for v(CN) and the azide stretches, taking the same estimates for angles as were used previously. The probable limits for the direction of the photo-active transition moment set by each dichroism observation are shown as shaded areas. In the diagram for the



Fig. 4. Planar conformations of 6. Estimates of the directions of the transition moments of v(CN) and the azide stretches are shown for each structure. The shaded areas define probable limits for the direction of the transition moment of the photoactive transition as derived from the dichroism of three IR bands: CN the v(CN) band, Az(as) the asymmetric azide stretch, Az(ps) the pseudo-symmetric azide stretch. See text for a discussion.

anti conformer, there is good overlap between the shaded areas for all three vibrations. Indeed, there are two separate regions where the photo-active transition moment could lie, labelled PA_1 and PA_2 in Fig. 4. In this case, therefore, the IR dichroism of $\nu(CN)$ and the azide stretches cannot determine the direction of the photo-active transition moment, even approximately. Nevertheless, although the direction of this transition moment is affected to some extent by the positions of substituents, it seems to lie fairly near the C(1)–N axis in the other cases studied, including 5 (see above). On this basis, there would be reason to prefer PA_1 as the most likely direction for the photo-active transition.

In the diagram for the syn conformer, there is also a reasonable degree of overlap of all three shaded areas, giving a possible direction of the photo-active transition moment shown as PA in Fig. 4. In the case of 6, therefore, the IR dichroism of the CN and azide stretches, taken alone, does not discriminate unequivocally between the syn and anti conformers. For the results to be consistent with the syn conformer, however, some very unlikely additional assumptions must be made. Firstly, moving the methyl group from the 2-position in 5 to the 6-position in 6 would have to rotate the photo-active transition moment through about 90°, which is unlikely for a substituent with only a weak electronic interaction. Secondly, the methyl group would have to have an attractive steric effect on the azide group in 6, but a repulsive effect in 5, which is inconsistent and even more unlikely. We can conclude, therefore, that azide 6 exists in N₂ matrices predominantly as the anti conformer, if the observed IR dichroism of this molecule is supplemented with additional evidence.

3.5. Limitations of the technique

The incorporation of cyano groups as *direction* labels into a group of flexible molecules - substituted phenyl azides – has allowed the conformations of these molecules trapped in low temperature matrices to be studied. For this purpose, the cyano group has several important advantages. It is linear, rigid and reasonably undemanding sterically. It has an IR absorption in a high-frequency and generally uncluttered region of the IR spectrum (approx. $2260-2210 \text{ cm}^{-1}$), and this v(CN) mode does not usually mix significantly with other molecular vibrations. Thus, to a good approximation, the direction of the transition moment of v(CN) can be assumed to lie along the C=N bond. Finally, it can be readily introduced into molecules by a variety of synthetic methods, and can be placed on tetrahedral, doubly bonded and triply bonded carbon.

Unfortunately, the insensitivity of the v(CN) frequency to molecular environment turned out to be too extreme in the examples we have investigated. In all cases, the v(CN) bands of starting

material and product were superimposed. This meant that the degree of polarization of these bands could not be determined. Conformational analysis of the azides had to be based on the direction of polarization of the v(CN) bands (parallel or perpendicular), which fortunately *could* be determined in each case, rather than on a more quantitative measure of dichroism.

The invariance of the v(CN) frequency is a drawback to the use of cyano groups in this type of study. A second disadvantage is that the transition moment of the $\nu(CN)$ absorption does not have a fixed directional relationship with the transition moment of the photo-active electronic absorption. Thus the observed polarizations of the various IR bands belonging to a molecule can be related to each other only through the photo-active absorption, and this introduces an extra element of uncertainty. Clearly, an ideal direction label would be a functional group possessing all the advantages of the CN group, but which also was the photo-active chromophore, with the electronic transition moment lying at a fixed and known angle within the group. In such an ideal case, the direction label might be eliminated or completely transformed upon photolysis, thus solving the band-overlap problem.

Despite the difficulties, the introduction of cyanide direction labels assisted in the identification of the predominant conformers of matrixisolated 2-, 3- and 4-cyanophenyl azides and two methyl-substituted derivatives. Analysis of the results by the graphical method of overlapping areas, as exemplified in Figs. 2 and 4, provides an easy way to assess the implications of combinations of dichroism observations. The method did not always lead to unequivocal discrimination between conformers, because of uncertainties in estimated directions of vibrational transition moments, particularly those of the azide group. The conclusions would be strengthened if the shaded areas in diagrams such as those shown in Figs. 2 and 4 could be narrowed down. This sharpening up of the data could be achieved (i) with better estimates of the directions of the transition moments of the asymmetric and pseudo-symmetric stretches of the azido group and (ii) with a more quantitative estimate of the experimental polarizations. This aim provides a stimulus for further study.

4. Conclusions

In this and the preceding paper [1], we have developed a method for identifying the predominant conformers of some flexible molecules cyano-substituted phenyl azides - trapped in low temperature matrices. The method utilizes photoselection of the trapped azides, to produce partially oriented samples exhibiting pronounced IR linear dichroism. The cyano groups were introduced as direction labels, in the hope that it would be possible to relate the direction of the $C \equiv N$ bond in each molecule to the directions of other bonds, especially those of the azido group. A graphical method of analysing the results in a qualitative, or at most semi-quantitative, way enabled conclusions to be drawn about the preferred conformers. The results suggest that the basic approach is quite sound, but the CN group suffers from the disadvantage that its stretching frequency is very insensitive to molecular environment, and band-overlap problems arose.

To a high degree of probability, we have determined that phenyl azides with one ortho substituent exist in N2 matrices predominantly as the anti conformer, i.e. with the azido group directed away from the ortho substituent. This was the case for 2-cyanophenyl azide [1], 3cyano-2-methylphenyl azide (5) and 3-cyano-6methylphenyl azide (6). In contrast. 3-cyanophenyl azide could not be photo-oriented in N₂ matrices to a significant or reproducible extent. This supports the expectation that the syn and anti conformers of this azide are virtually equal in energy and thus co-exist in comparable amounts.

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