Conformational Analysis by Matrix Photoselection

Ian R. Dunkin

Department of Pure and Applied Chemistry, University of Strathclyde, Cathedral Street, Glasgow G1 1XL. U.K.

Partial photolysis with plane-polarized light of phenyl azide in N_2 matrices at 12 K yields samples with dichroic i.r. spectra, analysis of which excludes C_{2v} and bisected-C_s geometries for phenyl azide, and suggests a planar-C_s or nearly planar conformation.

Partial photolysis with plane-polarized light of molecules trapped in a rigid medium leads, in favourable circumstances, to preferential decomposition of molecules having a particular orientation. In the resulting sample, the residual molecules of the starting material also have a preferred orientation, so that their vibrational and electronic spectra exhibit linear dichroism. The formation of dichroic samples in this manner is termed photoselection.[1] In the past few years, several papers have appeared describing photoselection of species trapped in low-temperature matrices.[2] In all cases, the species studied have been rigid molecules with at least C_{2v} symmetry. In this paper, we explore the possibility of using matrix photoselection coupled with i.r. dichroism as a means of determin-ing the conformation of a flexible molecule of lower sym-metry.

Phenyl azide (PhN_3) was chosen as a suitable compound for a variety of reasons. First, there has been considerable recent interest in the matrix photolysis of this and related azides.[3] Secondly, an almost complete vibrational assignment for PhN_3 has been proposed, based on its liquid-phase Raman spectrum.[4] Thirdly, the benzene ring has a collection of well documented i.r. bands, many of which are readily assignable.[5] Finally, the conformations of PhN_3 that need to be considered are limited simply to those attainable by rotation about the $C(1)-N(1)$ bond.

On the assumption of a bent arrangement of $C(1)-N(1)-N-$

(2), the PhN_3 molecule at its most symmetrical has C_s symmetry. The two conformations that are possible are: (i) the planar form (1), in which all the atoms lie in a plane that is also the symmetry-plane of the molecule, and (ii) the bisected form (2), in which the plane defined by C(6)–C(1)–C(2) is perpendicular to the plane defined by C(1)–N(1)–N(2), and in which the molecular symmetry-plane bisects the benzene ring through C(1) and C(4). Intermediate conformations have only C_1 symmetry.

In a C_{2v} monosubstituted benzene, the transition moment vectors of allowed transitions are of A_1, B_1, or B_2 symmetry [(3), (4), or (5), respectively]. If dichroism is induced in a sample of such a compound by photoselection involving an electronic transition of, for example, A_1 symmetry, the resulting i.r. spectrum will be such that the A_1 bands will have dichroism parallel to that of the electronic band ($I_\parallel < I_\perp$), while the B_1 and B_2 bands will have perpendicular dichroism ($I_\perp < I_\parallel$). When, as in (1) or (2), the symmetry is reduced to C_s, the vibrations divide into only two classes: A′ (in-plane) and A″ (out-of-plane). Transition moment vectors of A″ vibrations will be rigorously parallel to each other and perpendicular to those of A′ vibrations, but transition moment vectors of A′ vibrations may be at any angle with respect to each other. As an example, in conformation (1) of PhN_3, the out-of-plane deformation modes of the benzene ring, corresponding to B_1 vibrations in a C_{2v} phenyl derivative, will be of A″ symmetry; while in conformation (2) they will be of A′
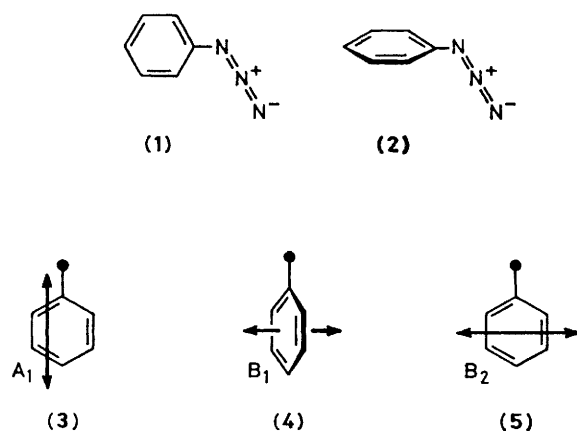
symmetry, and the A″ vibrations will be those corresponding to the B_2 vibrations of a C_{2v} phenyl derivative. Despite the rigorous division of the vibrations of (1) or (2) into only two symmetry classes, it was hoped that vibrational transition moment vectors in PhN_3 would retain directions more or less corresponding to those in a C_{2v} molecule. Thus, instead of A_1, B_1, and B_2 vibrations that are rigorously mutually perpendicular, there might be sets of more or less longitudinal (3), out-of-plane (4), or transverse (5) vibrations that define three roughly perpendicular directions within the molecule. When the symmetry of the molecule is reduced even further to C_1, there are no longer any symmetry restrictions on the directions of the transition-moment vectors. In the absence of detailed computations, any observed pattern of dichroism in the i.r. spectrum is consistent with C_1 symmetry. Qualitative dichroism observations cannot, therefore, exclude the possibility that the molecule has C_1 symmetry.

With these considerations in mind, we examined the polarized photolysis of PhN_3 isolated in N_2 matrices at 12 K

(1)   (2)

A_1 B_1 B_2

(3)   (4)   (5)
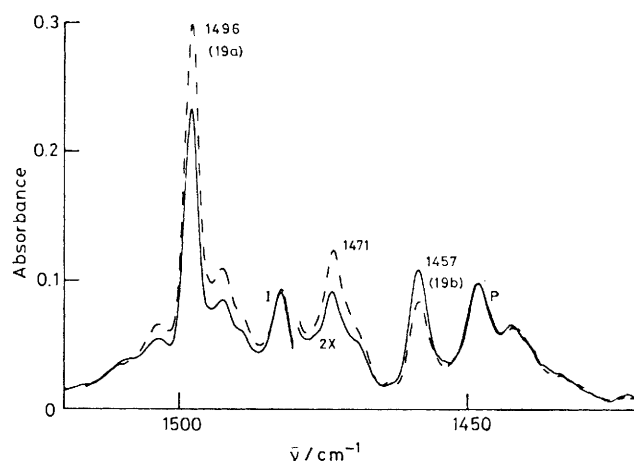
Figure 1. Part of the dichroic i.r. spectra of PhN_3 in N_2 at 12 K after incomplete photolysis (250 min) with x-polarized light. (———) x-polarized spectrum (parallel), (– –) y-polarized spectrum (perpendicular). Each spectrum is a computer average of four scans, and background subtraction has been carried out. Band assignments: I, impurity or overlap of PhN_3 and product bands; P, product bands; others belong to PhN_3.

Table 1. Frequencies, assignments, and dichroism of selected i.r. absorptions of PhN_3, following partial, polarized photolysis in N_2 at 12 K

Phenyl group vibrations				Azide group vibrations		
$\bar{v}/cm^{-1a}$	Assignment[b]	Symmetry type[c]	Dichroism[d]	$\bar{v}/cm^{-1a}$	Assignment[e]	Dichroism[d]
1598	8a	A_1	∥	2165—2087	$v(NNN)_{as}$	∥
1589, 1585	b	B_2	⊥	(7 bands)	Fermi resonance	
1496, 1491	19a	A_1	∥			
1457	19b	B_2	⊥	1305, 1298	$v(NNN)_s$	∥
1344, 1337	14	B_2	∥	670	$\delta(NNN)$	∥
1288, 1279, 1272	3	B_2	∥	537	$\gamma(NNN)$	⊥
1185	9a	A_1	∥			
1176	15	B_2	∥			
1076	18b	B_2	⊥			
1026	18a	A_1	∥			
751, 743	11	B_1	⊥			
687	4	B_1	⊥			

[a] Bands, calibrated against polystyrene film, are accurate to within ±2 cm⁻¹. [b] Nomenclature of Varsanyi (ref. 5). [c] In a phenyl group of C_{2v} symmetry. [d] Relative to that of the photoactive electronic absorption, (∥ parallel, ⊥ perpendicular). [e] Following ref. 4.

(matrix ratio 1 : 1000).† I.r. spectra (2200—400 cm^{-1}) of the matrices resulting from partial photolysis were recorded, with polarizations both parallel and perpendicular to the plane of polarization of the photolysis beam (see Figure 1)‡ The matrix i.r. spectrum of PhN$_3$ agreed reasonably closely with the liquid-phase Raman spectrum throughout the region examined but, at present, discussion will be limited to those i.r. bands of the phenyl group which are least sensitive to the nature of the substituent[5] and to four vibrations of the azide group.[4] These bands seem to be the most reliably assigned, and their frequencies and observed dichroism are given in Table 1.§ The most notable result is the fact that the bands corresponding to B$_2$ modes of a C_{2v} phenyl group do not all have the same dichroism. This observation excludes the possibility of a conformation having a symmetry plane perpendicular to the benzene ring, i.e. conformation (2) and the much less likely C_{2v} form. The remote possibility of a C_{2v} structure is also excluded by the fact that the band due to the azide deformation, δ(NNN), has the same dichroism as the azide stretching modes, ν(NNN)$_{as}$ and ν(NNN)$_s$. Rigorous inferences from the data cannot take us any further. Nevertheless, the complete loss of directional coherence found amongst the modes corresponding to B$_2$ vibrations in a C_{2v} phenyl

group strongly suggests that the conformation of PhN$_3$ more nearly resembles (1) than (2). This outcome is in accord with the results of Raman studies[6] of PhN$_3$ and a crystal structure determination for p-nitrophenyl azide,[7] both of which indicate planar or nearly planar conformations for these molecules.

The method of matrix photoselection, therefore, is capable of providing some information on the conformations of flexible molecules, although the limitations are severe. In particular, sets of bands with identical symmetry in, for example, a C_{2v} molecule cannot be relied upon to maintain roughly parallel directions when the symmetry is reduced.

---

† Matrix gas mixtures were prepared manometrically and condensed on a CsBr window at 12 K. The photolysis source was a 200 W high-pressure Hg arc, fitted with a water filter and Polacoat 105 UV WMR polarizer on a quartz substrate.

‡ I.r. spectra were recorded on a Perkin-Elmer PE 684 spectrometer interfaced with a Perkin-Elmer Infrared Data Station. Polarization of the sample beam was achieved by means of a SpecAc aluminium grid polarizer on a KRS-5 substrate.

§ Dichroism was observed for all but the weakest bands of PhN$_3$ and for some of the product bands. A fuller discussion of the spectra must be deferred, however, to a later publication.

References

1 A. C. Albrecht, Prog. React. Kinet., 1970, 5, 301.
2 See, for example, the following and references cited therein: J. J. Turner, J. K. Burdett, R. N. Perutz, and M. Poliakoff, Pure Appl. Chem., 1977, 49, 271; M. S. Baird, I. R. Dunkin, N. Hacker, M. Poliakoff, and J. J. Turner, J. Am. Chem. Soc. 1981, 103, 5190.
3 O. L. Chapman and J. P. Le Roux, J. Am. Chem. Soc., 1978, 100, 282; O. L. Chapman, R. S. Sheridan, and J. P. Le Roux, Rec. Trav. Chim. Pays-Bas, 1979, 98, 334; I. R. Dunkin and P. C. P. Thomson, J. Chem. Soc., Chem. Commun., 1980, 499.
4 R. Gaufrès and A. El Shahawy, C. R. Hebd. Seances Acad. Sci., Ser. C, 1975, 281, 503.
5 G. Varsanyi, 'Vibrational Spectra of Benzene Derivatives,' Academic Press, New York, 1969.
6 A. E. Shahawy and R. Gaufrès, J. Chim. Phys. Phys.-Chim. Biol., 1977, 74, 9.
7 A. Mugnoli, C. Mariani, and M. Simonetta, Acta Crystallogr., 1965, 19, 367.