

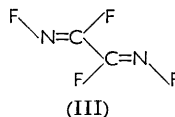
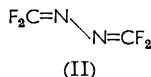
944. *The Infrared and Nuclear Magnetic Resonance Spectra of a Cyclic Perfluoroazo-compound.*

By E. A. V. EBSWORTH and G. L. HURST.

The infrared and nuclear magnetic resonance spectra of the compound $C_2F_4N_2$ strongly support the assignment of a cyclic azo-type structure; the infrared spectrum is analysed in terms of the vibrations expected of such a molecule.

THE compound $C_2F_4N_2$, obtained by treating cyanogen with silver(II) fluoride, decomposes to give nitrogen and tetrafluoroethylene, suggesting that the molecule has structure (I).¹ Other structures, however, such as (II) or (III), are consistent with the composition and the molecular weight; the infrared and nuclear magnetic resonance spectra of the compound have been recorded to obtain information about the structure by physical methods.

In the ring structure (I) it is likely that the ring would be at least approximately planar. The molecule is thus an asymmetric top belonging to the point group C_{2v} , with one plane of symmetry perpendicular to the C-C bond, another in the plane of the ring, and a two-fold axis along the junction of the planes. It is unusually difficult to estimate the probable



molecular dimensions, since very little information is available about the dimensions of similar molecules; for a range of possible bond lengths and angles, however [$d(C-C) = 1.55-1.60$, $d(C-N) = 1.45-1.50$, $d(C-F) = 1.33$, $d(N=N) = 1.20-1.30 \text{ \AA}$; $\angle FCF = 110-120^\circ$, $\angle FCC = 112-116^\circ$], the C -axis, associated with the greatest moment of inertia (I_C), is the two-fold axis; the B -axis, associated with the intermediate moment of inertia (I_B), is perpendicular to the plane of the ring; and the A -axis, associated with the least moment of inertia (I_A), is parallel to the C-C bond and in the plane of the ring. For what seem by analogy with molecules such as N_2F_2 ,² azomethane,³ and perfluorocyclobutane⁴ to be the best parameters [$d(C-C) = 1.60$, $d(C-N) = 1.475$, $d(C-F) = 1.33$, $d(N=N) = 1.25 \text{ \AA}$; $\angle FCF = 110^\circ$, $\angle FCC = \angle FCN$], $I_A = 171$, $I_B = 248$, $I_C = 258$ a.u., leading to values of the Badger and Zumwalt⁵ parameters S and ρ of about -0.8 and 0.5 . In molecules of this point group the principal axes coincide with the directions of the vibrational dipoles; thus vibrations giving dipole changes parallel to the A -axis would be expected to give vapour-phase infrared bands with type A contours (P , Q , and R branches of comparable intensity); those parallel to the B -axis, to give type B bands (P - R doublets with no central Q branch); and those parallel to the C -axis, to give type C bands (PQR structures with particularly prominent Q branches). For the values of S , ρ , and I_B given above, the expected P - R separations for bands of types A , B , and C can be estimated very roughly from Badger and Zumwalt's curves⁵ to be 13, 4.5, and 15 cm^{-1} , respectively. Expectations for structure (I) are summarised in Table I.

The point groups of structures (II) and (III) depend on the configuration about the central single bonds. For structure (II) the only forms with significant elements of symmetry are the planar *cis*- and *trans*-forms. The *cis*-structure, which is likely to be considerably strained, belongs to the point group C_{2v} (as does structure I), but in this case the C -axis is perpendicular to the molecular plane, the two-fold axis being the B -axis. Since the molecule is planar, all the bond stretching modes involve in-plane dipole changes,

¹ Emel us and Hurst, *J.*, 1962, 3276.

² Bauer, *J. Amer. Chem. Soc.*, 1947, **69**, 3104.

³ Boersch, *Sitzungsber. Akad. Wiss. Wien*, 1935, **144**, 1.

⁴ Lemaire and Livingstone, *J. Amer. Chem. Soc.*, 1952, **74**, 5732.

⁵ Badger and Zumwalt, *J. Chem. Phys.*, 1938, **6**, 711.

TABLE I.
Vibrations expected of the molecule (I) with their symmetry classes and associated band contours.

Approximate description of mode	Symmetry class				Approximate description of mode	Symmetry class			
	a_1	a_2	b_1	b_2		a_1	a_2	b_1	b_2
N=N stretching	ν_1				CF ₂ wagging	ν_6		ν_{14}	
C-F stretching	ν_2	ν_7	ν_{11}	ν_{16}	CF ₂ rocking		ν_8		ν_{17}
C-N stretching	ν_3		ν_{12}		CF ₂ twisting		ν_9		ν_{18}
C-C stretching	ν_4				Skeletal bending ...		ν_{10}	ν_{15}	
CF ₂ bending (scissors)	ν_5		ν_{13}						

Infrared band contour C. Inactive A B.

and so there should be no bands with type C contours at frequencies greater than 800—900 cm.⁻¹. The *trans*-form belongs to the point group C_{2v}; the a_g and b_g modes are forbidden in the infrared. The C-axis is again perpendicular to the plane of the ring; the in-plane modes should give bands with A/B hybrid contours, while here again there should be no bands with type C contours at frequencies higher than 800—900 cm.⁻¹.

There are several possible isomers of structure (III), differing in the arrangements of the CF and NF groups, in addition to the possibility of rotation about the C—C bond. The most symmetrical planar models belong to the point group C_{2v} or C_{2h}, depending on whether the nitrogen atoms are *cis* or *trans* to one another; their vibrations are likely to resemble those of the analogous forms of structure (II) so far as activity and band contours are concerned, though the frequency patterns are likely to be rather different. Here again it should be emphasised that for the planar forms there should be no bands with type C contours at frequencies greater than 800—900 cm.⁻¹.

In the fluorine resonance spectra, the equivalence of the fluorine atoms of structure (I) would be expected to lead to a single-line resonance; the equivalence is, however, destroyed by the presence of a single ¹³C atom, so the ¹³CF satellite resonances might show multiplet splitting. In structure (II), the same pairs of fluorine atoms remain *cis* and *trans* to one another for all angles of rotation about the N—N bond, so that the fluorine resonance spectrum would be expected to consist of two multiplet peaks, though the separation between the two might not be large. All isomers of structure (III) should give at least two resonances, which would be unlikely to coincide and should each show multiplet splitting. Thus it should be possible to distinguish between the ring structure and the others on the basis of infrared and nuclear magnetic resonance spectroscopy.

The Spectra.—(1) *Nuclear magnetic resonance.* The fluorine resonance spectrum consists of a single peak at $\phi = 102.5 \pm 0.5$ p.p.m., slightly broadened relative to the resonance of CCl₃F. Satellites were observed from ¹³CF₂ groups, with $J(^{13}\text{CF}) = 299 \pm 3$ c./sec.; the satellites showed multiplet splitting that was not found in the main peak, but the exact pattern could not be determined because the satellite resonances were too weak.

(2) *Infrared.* The frequencies of the observed bands in the vapour-phase infrared spectrum between 4000 and 270 cm.⁻¹ are given in Table 2, and the spectrum between 1550 and 400 cm.⁻¹ is shown in the Figure. Among the strong bands, associated with fundamentals, three types of contour can be distinguished, corresponding with the types A, B, and C bands of an asymmetric top molecule in which the vibrational dipoles coincide in direction with the principal axes of the molecule. The observed bands are therefore labelled A, B, or C in the Table, according to their contours (where these are resolved). The bands between 1500 and 700 cm.⁻¹ were studied under higher resolution to help to determine their contours. The mean P-R separations are: for type A bands, 14; for type B bands (only one resolved), 5—6; for type C bands, ~15 cm.⁻¹.

Discussion and Vibrational Assignments.—The observation of a single peak in the fluorine resonance spectrum is strong evidence in favour of the ring structure, and the chemical shift is in the range observed in other C—CF—N compounds.⁶ The suggestion of

⁶ Muller, Lauterbur, and Svatos, *J. Amer. Chem. Soc.*, 1957, **79**, 1807.

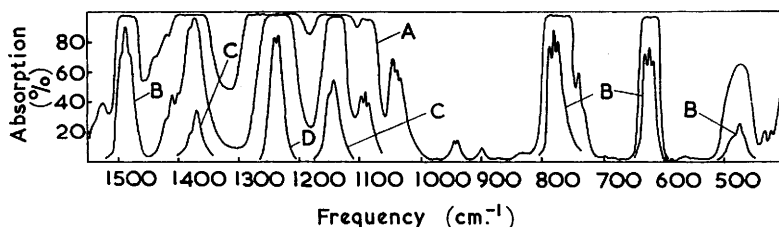
TABLE 2.

Observed infrared bands of $C_2F_4N_2$, and assignments on the basis of the ring structure.

Frequency (cm. ⁻¹)	Assignment	Frequency (cm. ⁻¹)	Assignment	Frequency (cm. ⁻¹)	Assignment
?285vw	? ν_{18}	~1030m	$\nu_5 + \nu_{18}$ (1029)	1840vw	$\nu_2 + \nu_6$ (1849)
397m ?A	ν_{15}	1045m C	ν_4	1885w	$\nu_3 + \nu_5$ (1887)
?427w		1094s A	ν_{12}	1995w	$\nu_2 + \nu_{14}$ (1999)
433w		1143vs C	ν_3	2040vw	$\nu_{11} + \nu_{14}$ (2034)
475m C	ν_6	1239vs B	ν_{16}	2125vw	$\nu_2 + \nu_5$ (2118)
?480m	? ν_{17}	1374vs C	ν_2	2150vw	$\nu_5 + \nu_{11}$ (2152)
565w	?2 ν_{18} (570)	1409s A	ν_{11}	2230vw	$\nu_1 + \nu_5$ (2228)
625m A	ν_{14}	1484vs C	ν_1	2270vw	$\nu_1 + \nu_{13}$ (2265)
744w C	ν_5	1523w	$\nu_5 + \nu_{13}$ (1525)	2370vw	$\nu_4 + \nu_{16}$ (2284)
781s A	ν_{13}	1562w	2 ν_{13} (1562)	2505w	$\nu_{11} + \nu_{12}$ (2503)
858w		1655w		2610w	$\nu_1 + \nu_3$ (2627)
903w	$\nu_2 - \nu_6$ (899)	1705w	$\nu_6 + \nu_{16}$ (1714)	2720w	$\nu_1 + \nu_{16}$ (2723)
945w	$\nu_6 + \nu_{17}$ (955)	1760vw	$\nu_3 + \nu_{14}$ (1768)		

Capital letters refer to type of band contour.

splitting in the satellite resonances that is not observed in the main peak is also in keeping with structure (I). Neither of the other structures would be expected to give this simple spectrum.



Trace of the infrared spectrum of tetrafluoro-3,4-dihydro-1,2-diazete (I), 1550—400 cm.⁻¹. The curves were recorded at the following pressures: (A) 200 mm.; (B) 25 mm.; (C) 4 mm.; (D) less than 1 mm.

The band contours in the infrared spectrum are in better accord with those expected of a molecule belonging to the point group C_{2v} than with the C_{2h} or any of the less symmetrical forms; moreover, the complexity of the spectrum helps to eliminate the centrosymmetric (C_{2h}) forms. This means that it is necessary to consider the ring structure, the planar *cis*-form of structure (II), and the symmetrical planar *cis*-forms of structure (III). In the last two cases, all the high-frequency modes involve in-plane dipole changes, and so all the bands at frequencies greater than ~ 900 cm.⁻¹ should give type A or B bands; for the ring compound, however, there should be four type C, two type A, and one type B bands in this region. Since four type C, one type B, and two type A bands are observed, the evidence very strongly favours the ring structure. This evidence (IV) is reinforced by the close agreement between the observed and the predicted *P-R* separations for the bands of all three types. The spectrum has therefore been analysed in terms of the vibrations expected of structure (I). The spectrum of the ring compound (IV) is available for comparison,⁷ but in that molecule the *C*-axis is perpendicular to the molecular plane; there are also six additional modes of vibration. There appear to be relatively few clear-cut analogies between the spectra of the two molecules; our assignments, which are given in Table 2, have therefore been based almost exclusively on the observed contours.

Of the 18 vibrational modes, 6 should be associated with type C bands, 5 with type A bands, and 3 with type B bands; 4 are inactive. Of the active modes, the four ring-stretching modes and the three (CF) stretching vibrations are all likely to appear at frequencies greater than 900 cm.⁻¹. The type C band at 1484 cm.⁻¹ clearly represents the

⁷ Nielsen, El-Sabban, and Alpert, *J. Chem. Phys.*, 1955, **23**, 324.

N=N stretching mode, ν_1 , and the type *B* band at 1239 cm^{-1} is due to the out-of-plane (CF) stretching mode, ν_{16} ; the type *C* bands at 1374 and 1143 cm^{-1} , and the type *A* bands at 1409 and 1094 cm^{-1} , are presumably associated with coupled (CF) and ring-stretching modes, but it is not possible to describe these vibrations in terms of the stretching of particular bonds. One other totally symmetric mode would be expected in this region; the weak band at 1045 cm^{-1} appears to have a type *C* contour, and so has been assigned to this vibration (ν_4).

The type *A* bands at 781 and 625 cm^{-1} are clearly associated with deformation modes. There is a weak but sharp *Q* branch at 744 cm^{-1} that may well represent the totally symmetric (CF₂) bending mode, ν_5 , while despite poor resolution at frequencies below 500 cm^{-1} a type *C* band can be distinguished at 475 cm^{-1} that is assigned to ν_6 . The remaining bands do not have clear-cut contours, and their assignment is less certain. There appears to be absorption at ~ 480 cm^{-1} in addition to the type *C* band at 475 cm^{-1} , there are two weak maxima separated by ~ 7 cm^{-1} and centred at 430 cm^{-1} , and there are a fairly strong and broad band at 397 cm^{-1} and, possibly, a weak band at 285 cm^{-1} . Of these, that at 397 cm^{-1} is too broad for a type *B* band and is probably due to the in-plane ring deformation mode (ν_{15}), which would be expected to give a type *A* band. The

TABLE 3.

Fundamental frequencies of tetrafluoro-3,4-dihydro-1,2-diazete (I).

Vibration	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_{11}	ν_{12}	ν_{13}	ν_{14}	ν_{15}	ν_{16}	ν_{17}	ν_{18}
Frequency ...	1484	1374	1143	1045	744	475	1409	1094	781	625	397	1239	480	285

maxima close to 430 cm^{-1} might represent the *P* and the *R* branches of a type *B* band and so might be due to the CF₂ rocking mode, ν_{17} , but they do not look like components of a single band; we have assigned the value of ~ 480 cm^{-1} to this mode, because of the distorted envelope of the type *C* band there. Similarly, although we have assigned the band at 285 cm^{-1} to the remaining active vibration, the CF₂ twisting mode, the band may possibly be spurious, so the last two assignments must be regarded as tentative. The infrared-active fundamental frequencies are given in Table 3.

Despite some minor uncertainties, the ease with which the observed infrared frequencies can be accounted for in terms of the vibrations expected of the ring model, together with the agreement between observed and predicted band contours and branch separations and the simple nuclear magnetic resonance spectrum, go far towards establishing the ring structure for the molecule.

Experimental.—The preparation of the compound is described elsewhere;¹ the purity of samples used in this study was tested by measurements of vapour density and by gas-phase chromatography. The nuclear magnetic resonance spectra were obtained with a Varian Associates V4300 spectrometer, operating at 40 Mc./sec. Spectra were recorded of the liquid containing a drop of trichlorofluoromethane as internal standard, and of $\sim 5\%$ solutions (by weight) in the same substance as solvent; the value of ϕ given⁸ is the mean of three measurements of the dilute solution, the dilution shift being less than 10 c./sec.

The infrared spectra between 4000 and 270 cm^{-1} were recorded by means of a Perkin-Elmer model 21 double-beam spectrometer, fitted with a sodium chloride, a potassium bromide, or a caesium bromide prism; the sample was contained in 100 mm. cells in the gas phase. The spectrum between 1550 and 700 cm^{-1} was also recorded by using a Grubb-Parsons G.S.2 grating instrument to help to establish the band-contours.

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UNIVERSITY CHEMICAL LABORATORIES,
LENSFIELD ROAD, CAMBRIDGE.

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⁸ Filipovitch and Tiers, *J. Phys. Chem.*, 1959, **63**, 761.