Spectrochimica Acta, Vol. 48A, No. 5, pp. 659–669, 1992
Printed in Great Britain

0584-8539/92 $5.00 + 0.00

Infrared studies of conformational isomerism in some *gem*-chloronitrosoalkanes

K. M. EVANS, S. J. IRESON and M. R. S. MCCOUSTRA*
School of Chemical Sciences, University of East Anglia, Norwich NR4 7TJ, U.K.

and

J. PFAB
Department of Chemistry, Heriot-Watt University, Edinburgh EH14 4AS, U.K.

(*Received* 15 *August* 1991; *in final form* 5 *October* 1991; *accepted* 8 *October* 1991)

Abstract—The IR spectra of 2-chloro-2-nitrosopropane, 2-chloro-2-nitrosobutane and 2-chloro-3-methyl-2-nitrosobutane have been studied in the gas phase and solid phase, and in solutions of varying polarity. The spectra reveal clear evidence for the hindered internal rotation of the NO functional group about the C–N bond in a splitting of the N=O stretching band. The spectra can be interpreted as arising from energetically favoured *cis* conformational isomers, exhibiting the higher of the observed N=O stretching frequencies. In each case, assignment of the lower N=O stretching frequency is uncertain on the basis of experimental evidence. The results of semi-empirical molecular orbital calculations, however, support the assignment of this feature to the *gauche* conformational isomers. Temperature dependent IR spectroscopy has been employed in the determination of conformational enthalpy differences in both the gas phase and non-polar solution, which are then compared to the results of semi-empirical molecular orbital calculations.

INTRODUCTION

MOLECULAR conformation can have a significant effect on the reactivity of chemical species. This is superbly illustrated by the "lock and key" behaviour of the reactants in enzyme catalyzed biochemical transformations. Therefore, the determination of molecular conformation, either by experimental or theoretical means, and the influence of phase, temperature, solvent polarity etc. on conformation can have a profound influence on our understanding of the structural aspects of chemical reactivity in such systems. The study of such large systems has, of course, been revolutionized in the past decade through the development and application of two-dimensional nuclear magnetic resonance techniques [1, 2], and in particular those which make use of the nuclear Overhauser effect [1, 3]. While such studies can readily answer the question of protein and nucleotide conformation, the underlying question as to why such a macromolecule should adopt a particular conformation remains unanswered. Fundamental studies of the conformational behaviour of small molecules are of the greatest relevance in pursuing the answer to this question.

A wide variety of methods, ranging from analysis of thermodynamic data to neutron and electron scattering and running through a wide gamut of techniques which rely on the interaction of the molecule with electromagnetic radiation of one form or another, have been applied to the investigation of molecular conformation [4, 5]. Infrared spectroscopy has proved to be a particularly fruitful technique, in allowing investigations to be performed in a variety of phases (solid, liquid and gas) and a wide range of temperatures. In the far-IR, it has proved possible to observe directly the torsional vibrations of small molecules [6–9]. In the mid-IR, studies based on the observations of small shifts in vibrational frequencies between different conformational isomers (conformers) have proved equally valuable [10, 11]. Such investigations are more favourable for simple groups, such as the hydroxyl and nitroso functions, where any complicating effects associated with the coupling of torsional vibrations and other low frequency out-of-plane modes are minimized and where stretching features in the IR are isolated. The

---

* Author to whom correspondence should be addressed.

latter ensuring any complications associated with band overlap in the fingerprint region are removed. Much of the work on OH torsion has been discussed in the recent paper of BELHEKAR *et al.* [11] and the work on NO torsion in simple aliphatic *C*-nitroso compounds has been reviewed by MCCOUSTRA and PFAB [12].

The latter have proved to be a particularly interesting case. Simple steric considerations would suggest the favouring of staggered conformers. However, experimental observations on a number of nitrosoalkanes have indicated that eclipsed conformations are preferred [12]. This behaviour is a consequence of strong intramolecular electronic interactions, and cannot be adequately represented in the simple force fields used in molecular mechanics calculations. Consequently, such calculations fail to adequately predict the conformational behaviour of nitrosoalkanes. If such models are therefore to be used to predict the conformational behaviour of nitrosoalkanes with any degree of certainty, experimental and higher order theoretical studies of this behaviour must be suitably parameterized. In the work described below, IR spectroscopy and semi-empirical molecular orbital calculations have been used to study the conformational equilibria in a number of *gem*-chloronitrosoalkanes in the gas, solid and liquid phases, in an effort to provide the necessary data for such parameterization.

EXPERIMENTAL

The compounds under study [2-chloro-2-nitrosopropane (**I**), 2-chloro-2-nitrosobutane (**II**) and 2-chloro-3-methyl-2-nitrosobutane (**III**)] were prepared from appropriate oximes (0.05 mole of either acetone oxime, methyl ethyl ketone oxime or methyl isopropyl ketone oxime) by direct chlorination under aqueous conditions [13, 14]. The products, volatile blue liquids, were separated and washed with sodium hydrogen carbonate solution and distilled water, prior to a brief centrifugation to remove residual water. These materials were then degassed on a glass vacuum line, by repeated application of freeze–pump–thaw cycles, and finally purified by trap-to-trap distillation.

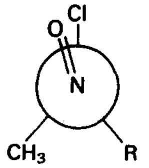
Acetone oxime (Aldrich) was used as supplied. The remaining precursors were prepared from the appropriate ketone (1 mole) by reaction with hydroxylamine hydrochloride (1 mole) and sodium hydrogen carbonate (1 mole) in water (*ca* 250 cm^3) under reflux. After separating the organic layer, washing with water and drying over anhydrous sodium sulphate, the oximes were recovered by fractional distillation of the crude material at atmospheric pressure. Methyl ethyl ketone oxime was collected as a fraction distilling over at around 150°C (literature boiling point 152–153°C [15]) and methyl isopropyl ketone oxime as a fraction at around 158°C (literature boiling point 157–158°C [15]).

The infrared spectra were obtained on a variety of dispersive and Fourier transform IR spectrophotometers including a Perkin–Elmer PE580 and a Mattson Polaris. Typically, spectra were recorded at a resolution of 1 cm^{-1}. Gas phase spectra were recorded for samples contained in a 10 cm path-length variable temperature gas cell equipped with potassium bromide windows (Specac). Low temperature, solid phase spectra were recorded using a simple liquid nitrogen cooled cryostat equipped with a potassium bromide dosing plate and potassium bromide windows. Room temperature liquid phase spectra were obtained using a pair of matched sodium chloride liquid cells. Variable temperature liquid phase studies were performed in a similar cell adapted for heating with a circulating water heater. Spectroscopic grade solvents (Aldrich) were used in all liquid phase studies.

Semi-empirical molecular orbital calculations were performed on a DEC Vax 8650 using the AMPAC package [16]. Initial molecular geometries were generated from data on existing molecules of the same type and from standard tables of bond lengths. Complete geometric optimization calculations were performed using the MNDO algorithm [17–21] at 10° intervals of the torsional angle. The latter being the only fixed geometric parameter in each calculation.

RESULTS AND DISCUSSION

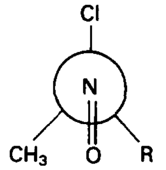
In the discussion that follows, the conformers illustrated in Fig. 1 will be considered. Steric factors alone would suggest a preference for staggered conformations, including the *trans*. However, extrapolation of the behaviour of the substituted nitrosomethanes to



Cis

Gauche

Staggered



Trans

Fig. 1. Conformational isomers of *gem*-chloronitrosoalkanes discussed in this paper: R = CH_3(I), CH_2CH_3(II) and $CH(CH_3)_2$ (III).

the present case would suggest that eclipsed (*cis* and *gauche*) conformers would predominate. Infrared evidence, as presented below, supports this contention.

2-*Chloro-2-nitrosopropane*

The mid-IR spectrum of a neat liquid film of I is readily assigned by comparison with that of 2,2-dichloropropane [22–25]. With the reduction in symmetry from C_{2v} to C_s, the 30 normal modes of I can be assigned to a′ and a″ symmetries. There are 17 of the former and 13 of the latter. Of the 30 normal modes, six are CH_3 stretching modes, six are CH_3 deformation, four are CH_3 rocking, two are CH_3 torsion and nine are associated with the skeletal stretch and deformation. The details of this assignment are not, however, relevant to this discussion and have been discussed previously [26]. The replacement of one of the chlorine atoms by the nitroso group has little effect on the vibrational characteristics of the hydrocarbon backbone of the molecule, but will give rise to three additional vibrational modes. The first of these is the N=O stretching vibration, which is assigned to the strong band centred around 1580 cm^{-1}. The remaining modes, the CNO bending vibration and the torsional mode, are expected to lie below the 600 cm^{-1} cut-off of the sodium chloride plates [12, 27–29]. By comparison with analogous compounds, the latter is expected to lie below 100 cm^{-1} [12, 27, 29].

Figure 2(a) shows the N=O stretching band in more detail. The band is clearly split, with a high frequency maximum at 1587 cm^{-1} and, a somewhat weaker low frequency maximum at 1570 cm^{-1}. For comparison, the N=O stretching band of a thin film deposited on a potassium bromide plate at around 80 K is shown in Fig. 2(b). The absence of the low frequency band in the latter is taken as evidence that, in the neat liquid, **I** exhibits conformational isomerism. The predominant conformer being that which gives rise the high frequency band at 1587 cm^{-1}. The detailed assignment of the two N=O stretching bands can be made by comparison with analogues, by an analysis of the rotational band contours of gas phase spectrum [Fig. 2(c)], by interpretation of the solvent polarity dependence of the peak absorbances and by semi-empirical MO calculations.

In CH_3NO and CF_3NO, the weight of evidence from a variety of studies clearly indicates that in the ground electronic state the most stable conformation is eclipsed [12]. With $CClF_2NO$ and CCl_2FNO, the evidence supports this, but further suggests that in such an asymmetric case the most stable conformer is that in which the most electronegative atom is eclipsed [12]. Extrapolating this behaviour to **I** would suggest that the *cis* conformer is most stable and is therefore associated with the stronger 1587 cm^{-1} N=O stretching band. The weaker, lower frequency band can therefore be assigned to the N=O stretch of the *gauche* conformer.

Prior to considering the rotational contours of the gas phase N=O stretching band, the rotational properties of the various conformers must be considered. These are best described in terms of Ray asymmetry parameters (κ). The *cis* conformer, with a κ value of 0.08, is highly asymmetric and would be expected to exhibit a hybrid band contour of the AB-type. The *gauche* ($\kappa = 0.79$) and *trans* ($\kappa = 0.90$) are near prolate symmetric tops and would possess A-type band contours with small contributions from B-type (*gauche* and *trans*) and C-types (*trans*) contours. The observed contours are consistent with the

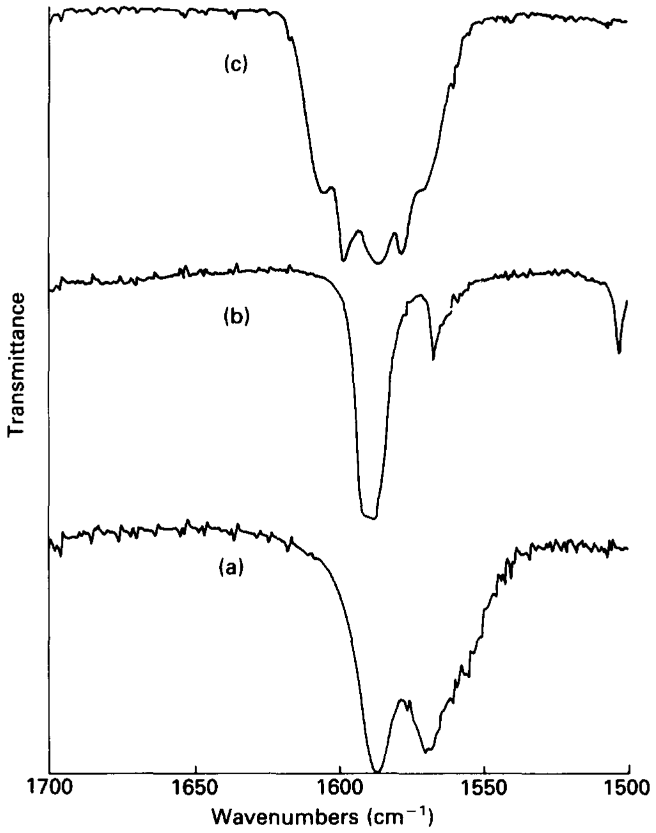


Fig. 2. The N=O stretching region of the mid-IR spectrum of 2-chloro-2-nitrosopropane (**I**): (a) in neat liquid, (b) in the solid at 80 K and (c) in the gas phase at room temperature.

Table 1(a). Absorbance ratio* of the N=O stretching bands as a function of solvent

Solvent	Molecule I	II	III
Cyclohexane	1.35	1.58	0.76
Chloroform	1.51	2.40	2.32
Acetonitrile	1.61		2.74

* Defined as the ratio of the absorbance of the *cis* peak divided by that of the *gauche*.

Table 1(b). Dipole moments calculated by MNDO for various conformations of **I** and **II**

Solvent	Molecule I	II
Cis	2.311 D	2.346 D
Methyl *gauche*	2.237 D	2.282 D
Ethyl *gauche*		2.287 D
Trans	2.235 D	2.287 D

1 D ≈ 3.336×10^{-30} Cm.

assignment of the 1587 cm^{-1} band to the *cis* conformer. The low frequency band cannot, however, be assigned conclusively to either the *gauche* or the *trans* conformer on this basis.

The solvent dependence of the N=O stretching band in **I** is illustrated in Table 1(a). It is clear from this study, that as the solvent polarity increases, the preference for the conformer possessing the higher N=O stretching frequency increases. This can be explained by considering the dipole moments of the various conformers in Table 1(b), which have been calculated using the MNDO algorithm within AMPAC. As the solvent polarity is increased, it can be argued that the more polar conformer would be stabilized. Thus, the high frequency N=O stretching band can be assigned to the *cis* conformer, as above, and the lower frequency band to either *gauche* or *trans*.

The final evidence supporting the assignment proposed above comes from semi-empirical MO calculations. The result of an MNDO calculation of the torsional potential of **I** is shown in Fig. 3(a). The deep well at 0° (360°) is associated with the *cis* conformer, while the shallow minimum at *ca* 120° (240°) is associated with the *gauche*. As further evidence supporting this assignment, semi-empirical force field calculations were performed using the AMPAC package. The results of these calculations are summarized in Table 2. Typically the calculated vibrational frequencies are 700–800 cm^{-1} higher than that observed experimentally. This, however, is not important as it only reflects deficiencies in the semi-empirical force field calculation. The order of the N=O stretching frequencies calculated for the *cis* and *gauche* conformers is, however, important and strongly supports the proposed assignment.

The calculations have also made available optimum geometries for the various conformations of **I**. The most significant of these parameters are summarized in Table 3. It is clear from these data that as the oxygen atom is rotated away from the chlorine atom, some significant structural relaxation occurs. The N–O and C–N band lengths increase, and the CNO bond angle closes slightly, while the C–Cl band shortens and the NCCl band angle decreases significantly. Such changes are as expected given the steric interactions in the planar eclipsed ClCNO frame.

Variable temperature IR studies were performed in both the gas phase and in cyclohexane solution on **I**. Consider the equilibrium between two conformers of a

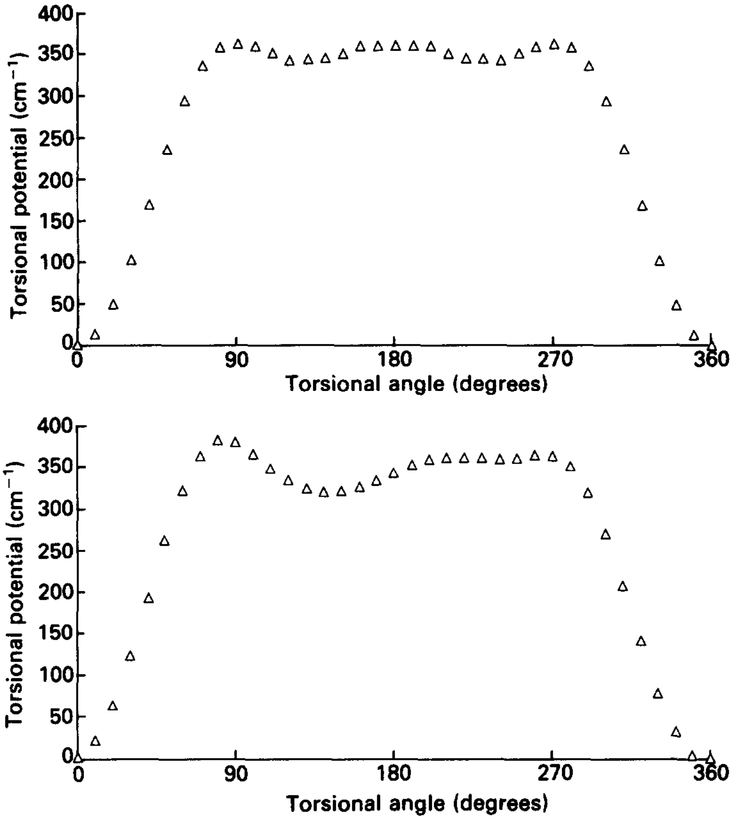


Fig. 3. Torsional potential evaluated using the MNDO algorithim of the AMPAC semi-empirical molecular orbital package (see text) for (a) 2-chloro-2-nitrosopropane (I) and (b) 2-chloro-2-nitrosobutane (II). [1 cm^{-1} ≈ 11.96 J mol^{-1}.]

molecule,

$$A \rightleftharpoons B \tag{1}$$

where the equilibrium constant is given by

$$K=\frac{[B]}{[A]}. \tag{2}$$

If then, as in the present situation, each conformer exhibits a spectroscopically distinct feature, the Beer–Lambert Law can be employed to determine the concentrations of each conformer. The Van't Hoff isochore can then be employed in the analysis of the

Table 2. Frequencies of the N=O stretching vibration

		Molecule	
	$\tilde{\nu}$/cm^{-1}	I	II
Cis	Observed	1587	1584
	Calculated	2327.2	2327.6
Methyl *gauche*	Observed	1570	1565*
	Calculated	2320.9	2321.6
Ethyl *gauche*	Observed	—	1565*
	Calculated	—	2322.5
$\Delta\tilde{\nu}$/cm^{-1}	Observed	17	19
	Calculated	6	6.3 and 5.3

* The low frequency N=O stretch in **II** cannot be resolved.

Table 3. Optimum geometric parameters for some *gem*-chloronitrosalkanes obtained from MNDO calculations

	I			II			
Parameter	*Cis*	*Gauche*	*Trans*	*Cis*	Methyl *gauche*	Ethyl *gauche*	*Trans*
$R_{N\text{-}O}$/Å	1.1560	1.1572	1.1580	1.1559	1.1571	1.1569	1.1579
$R_{C\text{-}CC}$/Å	1.8233	1.8214	1.8212	1.8238	1.8221	1.8223	1.8221
$R_{C\text{-}NO}$/Å	1.5156	1.5234	1.5220	1.5202	1.5275	1.5270	1.5261
$R_{C\text{-}Me}$/Å	1.5455	1.5415*	1.5435	1.5458	1.5420	1.5449	1.5440
$R_{C\text{-}R}$/Å	1.5455	1.5445*	1.5444	1.5567	1.5557	1.5525	1.5549
<NCCl/deg	112.60	101.02	101.06	111.85	100.21	100.05	100.23
<CNO/deg	121.25	119.92	119.27	121.30	102.02	120.47	119.49
<NCMe/deg	107.69	107.92*	107.87	107.62	107.77	108.68	107.74
<NCR/deg	107.69	108.74*	107.64	109.04	110.16	109.24	109.13

* $R_{C\text{-}Me}$ and <NCMe refer to the eclipsed methyl group in this conformation while $R_{C\text{-}R}$ and <NCR refer to the other methyl group.

temperature variation of K obtained from an analysis of the temperature variation of the IR spectrum using Eqn (3) [4, 10], where A_i is the absorbance of a particular conformer:

$$\log_e \frac{A_B}{A_A} = -\frac{\Delta H}{RT} - \frac{\Delta S}{R} - \log_e \frac{\varepsilon_A}{\beta_B}. \tag{3}$$

If either of the conformers exhibit degeneracy, as for example the double degeneracy of the *gauche* conformer in **I**, an additional term is added to Eqn (3) reflecting this,

$$\log_e \frac{A_B}{A_A} = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} - \log_e \frac{\varepsilon_A g_B}{\varepsilon_B g_A} \tag{4}$$

where g_i are the relevant degeneracies. The value of ΔH thus obtained represents that enthalpy difference between the two conformers. In the present study, this is the difference between the *gauche* and *cis* conformers as assigned above ($\Delta_{g\text{-}c}H$). The value of $\Delta_{g\text{-}c}H$ is readily obtained from the MNDO torsional potential in Fig. 3(a). Experimental measurements, made over a 50°C temperature range from 15°C, are summarized in Fig. 5 and presented in Table 4. The temperature range employed was limited due to solvent evaporation in the solution phase work and to thermal decomposition of **I** on the walls of the stainless steel gas cell. Evidence for this decomposition was to be found in the observation of a strong absorption feature at around 1820 cm^{-1} which was associated with nitrosyl chloride. The agreement between the NMDO value and the cyclohexane solution value is remarkable. The gas phase data are, however, significantly different. This can be readily explained, however, by recognizing that in the gas phase, raising the temperature will lead both to an increase in peak absorbance and to a

Table 4. Conformational enthalpy differences

	Molecule	
$\Delta H_{g\text{-}c}$/kJ mol^{-1}*	I	II
Calculated	4.10	3.97 (methyl *gauche*) 4.28 (ethyl *gauche*)
Gas phase	0.78 ± 0.19	0.96 ± 0.12
Cyclohexane solution	4.50 ± 0.56	3.24 ± 0.33

* The enthalpy difference between the higher energy *gauche* conformer and the lower *cis* conformer.

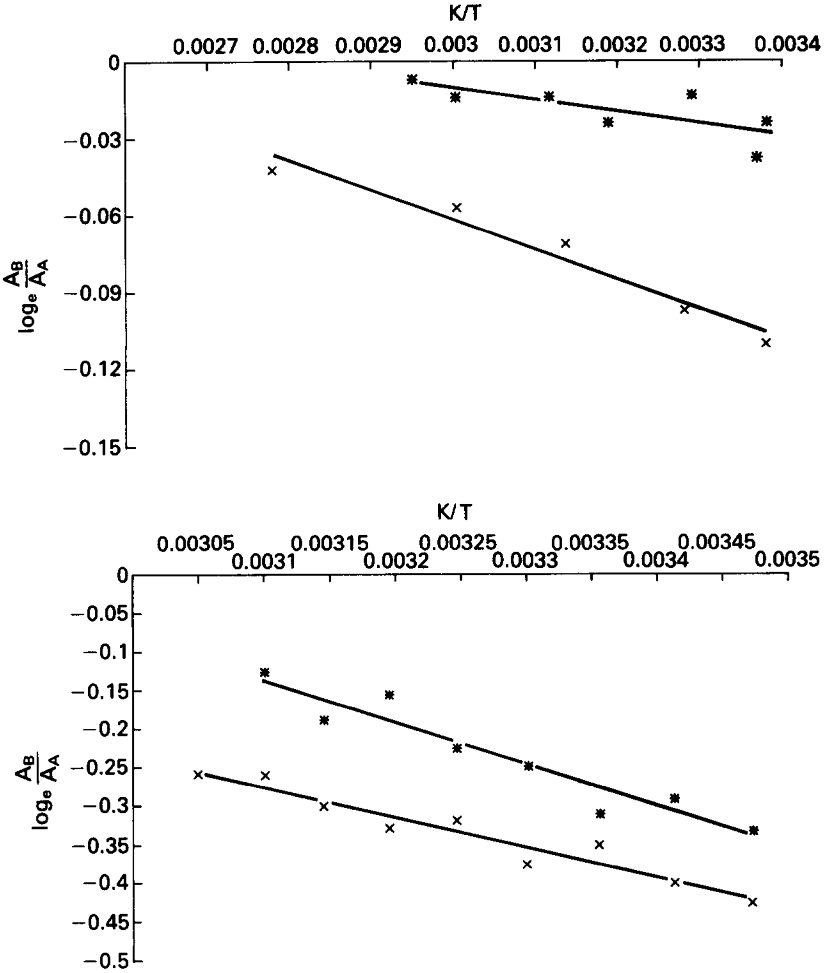


Fig. 4. Plots of $\log_e A_B/A_A$ against K/T for (a) gas phase 2-chloro-2-nitrosopropane [*] and 2-chloro-2-nitrosobutane [×], and (b) dilute cyclohexane solutions of 2-chloro-2-nitosopropane [*] and 2-chloro-2-nitrosobutane [×]. The straight lines represent the least squares fit of Eqn (4) to these data. The resulting enthalpy differences are summarized in Table 4.

significant broadening of the rotational band contour. The latter does not occur in solution. Ideally, in the case of the gas phase work, integrated band areas should be considered and not peak absorbances. The complexity of the band contours prevented such a detailed analysis in the present study. Consequently, the acceptable value of $\Delta_{g-c}H$ for **I** is that obtained from the study in cyclohexane solution.

2-*Chloro*-2-*nitrosobutane*

The IR spectrum of **II** resembles both that of **I** and 2,2-dichlorobutane [30, 31]. The N=O stretching band is clearly split [Fig. 5(a)] as in **I**. The assignment of the two components of the N=O stretching band can be made with similar arguments to above. Extrapolating the behaviour of **I**, the *cis* conformer would be expected to be the most stable and associated with the higher frequency 1584 cm^{-1} band. The *gauche* conformer would be assigned to the lower frequency 1565 cm^{-1} band. Naturally, there are two distinguishable *gauche* conformers in this system. The vibrational frequencies calculated using AMPAC, however, are only separated by 0.9 cm^{-1} (Table 2) and it is unlikely that they could be spectrally resolved. The lower frequency band, therefore contains contributions from both the methyl *gauche* and the ethyl *gauche*. This assignment is supported by both the behaviour in solvents of increasing polarity, where the more polar

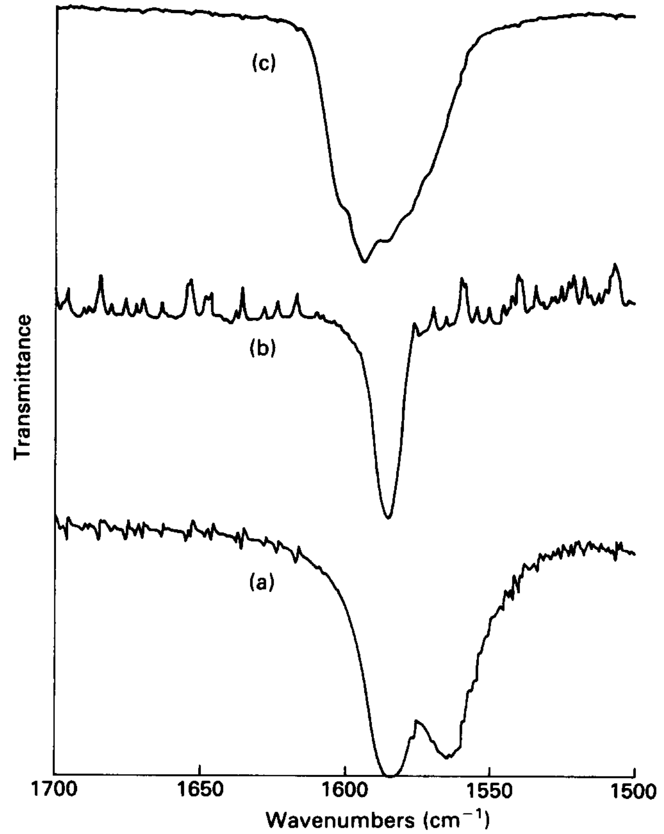


Fig. 5. The N=O stretching region of the mid-IR spectrum of 2-chloro-2-nitrosobutane (**II**): (a) in neat liquid, (b) in the solid at 80 K and (c) in the gas phase at room temperature. (Note that the negative water absorptions in (b) reflect the use of an unpurged spectrophotometer in performing these measurements, and consequent miscancellation of water absorptions.)

the solvent the greater the preference for the *cis* conformer (Table 1), and by the calculated torsional potential shown in Fig. 3(b).

The calculated torsional potential gives enthalpy differences $\Delta_{g-c}H$ between the conformers of around 4 kJ mol^{-1}. These are listed in Table 4. Variable temperature IR spectroscopy with a Van't Hoff isochore analysis (Fig. 4) gives enthalpy differences of 0.96 and 3.24 kJ mol^{-1} in the gas phase and in cyclohexane, respectively. The agreement between the calculated and non-polar solution phase spectrum is again quite remarkable. The low value for the gas phase is readily accounted for using the arguments previously presented. The solution phase result is obviously the more acceptable value for $\Delta_{g-c}H$ in the light of these comments.

The geometric data obtained from the MNDO calculations are summarized in Table 3. The behaviour around the ClCNO frame is similar to that of **I**.

2-*Chloro*-3-*methyl*-2-*nitrosobutane*

The low vapour pressure of **III** meant that the gas phase spectrum could not be recorded. The spectrum of the neat liquid film is similar to those of **I** and **II**, with a distinctive splitting of the N=O stretch band to yield a high frequency band at 1581 cm^{-1} with a low frequency shoulder at 1575 cm^{-1}. Again, as in the case of **I** and **II** but in contrast to the neat liquid film, the spectrum of the thin solid film at 80 K presented a single narrow feature at 1582 cm^{-1}. The behaviour in solvents of increasing polarity is also identical to that of the other compounds in the study, although the data indicate an even stronger preference for the higher frequency conformer, as in the case of **I** and **II**.

CONCLUSION

The IR study of **I**, **II** and **III** has clearly illustrated the existence of conformational isomerism in these compounds and confirms, in the case of **I**, the previously published work of TREPALIN *et al.* [26, 32]. The splitting of the N=O stretching band, at temperatures above 80 K, is quite consistent with this isomerism. A detailed analysis of the band, its temperature dependence and solvent dependence leads to the conclusion that the *cis* conformational isomer is energetically the most stable and predominates at room temperature in the gas and liquid phases. Experimental evidence presented here does not, however, permit a definite assignment of the minor conformational isomer.

In recent publications, TREPALIN *et al.* [26, 32] have presented evidence from far-IR studies and MNDO calculations that lend support to the suggestion that the *trans* conformation is the lesser component. The assignment of far-IR spectra, such as in [32], is complicated by strongly absorbing contaminants from the preparation of **I**, such as water and hydrogen chloride, and from the decomposition of **I** on gas cell walls, such as nitrosyl chloride and acetone. The latter, however, do not appear to have been considered in assigning the reported spectra. Furthermore, the analysis of such data using torsional energy level calculations is very sensitive to the choice of geometric and potential parameters, as discussed in MCCOUSTRA and PFAB [12] and in references contained within that work. The results of calculations presented here support an alternative assignment of the lesser component to the *gauche* conformation in both **I** and **II**, and by implication **III**. Similar calculations on dichloronitrosomethane [33] and 2-nitrosopropane [34] support this assignment. Clearly the question of the nature of the lesser conformational isomer remains somewhat open. The calculated enthalpy difference for **I** obtained in the present work is consistent with that previously reported [26, 32] given the argument in the text.

Acknowledgements—One of us (MRSMcC) would like to thank the Carnegie Trust for the Universities of Scotland for a vacation scholarship under which some of the work described above was initially performed.

REFERENCES

[1] M. P. Williamson, *Chem. Brit.* **27**, 335 (1991).
[2] K. Wüthrich, *NMR of Proteins and Nucleic Acids.* John Wiley, New York (1986).
[3] D. Neuhaus and M. P. Williamson, *The Nuclear Overhauser Effect in Structural and Conformational Analysis.* VCH, New York (1989).
[4] W. J. Orville-Thomas, *Internal Rotation in Molecules.* John Wiley, New York (1974).
[5] D. G. Lister, J. N. Macdonald and N. L. Owen, *Internal Rotation and Inversion.* Academic Press, New York (1978).
[6] H. C. Silver and J. L. Wood, *Trans. Faraday Soc.* **60**, 5 (1964).
[7] W. G. Fateley, R. K. Harris, F. A. Miller and R. E. Witkowski, *Spectrochim. Acta* **21**, 231 (1965).
[8] F. A. Miller, W. G. Fateley and R. E. Witkowski, *Spectrochim. Acta* **23A**, 891 (1967).
[9] G. M. Bradley and H. L. Strauss, *J. Phys. Chem.* **79**, 1953 (1975).
[10] J. J. Turner, M. Poliakoff, S. M. Howdle, S. A. Jackson and J. G. McLaughlin, *Faraday Disc. Chem. Soc.* **86**, 271 (1988).
[11] A. A. Belhekar, M. S. Agashe and C. I. Jose, *J. Chem. Soc. Faraday Trans* **86**, 1781 (1990).
[12] M. R. S. McCoustra and J. Pfab, *Spectrochim. Acta* **46A**, 937 (1990).
[13] G. Ponzio, *Chem. Zentrallblatt* **10**, 1692 (1906).
[14] M. Kosinski, *Lodz. Towarz. Nauk., Wydzial III, Acta. Chim.* **9**, 93 (1964).
[15] *Handbook of Chemistry and Physics,* 55th Edn. CRC Press, Cleveland (1974).
[16] *AMPAC, QCPE No.* 506, Quantum Chemistry Program Exchange, Department of Chemistry, Indiana University, Bloomington, Indiana 47405, U.S.A.
[17] M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4899 (1977).
[18] M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4907 (1977).
[19] M. J. S. Dewar and M. L. McKee, *J. Am. Chem. Soc.* **99**, 5231 (1977).
[20] M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.* **100**, 777 (1978).
[21] M. J. S. Dewar and H. S. Rzepa, *J. Am. Chem. Soc.* **100**, 784 (1978).
[22] P. Klaboe, *Spectrochim. Acta* **26**, 977 (1970).
[23] J. H. S. Green and D. J. Harrison, *Spectrochim. Acta* **27A**, 1217 (1971).
[24] D. C. McKean and B. W. Laurie, *J. Molec. Struct.* **27**, 317 (1975).

[25] G. Berlandier, J. L. Bribes, R. Gaufres and V. Tabacik, *J. Chim. Phys. Phys.-Chim. Biol.* **75**, 202 (1978).
[26] S. V. Trepalin, A. V. Yarkov, V. B. Sokolov, A. N. Ivanov, N. A. Aksinenko and V. I. Fetisov, *Izv. Akad. Navk. SSSR, Ser. Khim.* **7**, 1538 (1989).
[27] H. F. Shurvell, S. C. Dass and R. D. Gordon, *Can. J. Chem.* **53**, 3149 (1974).
[28] A. J. Barnes, H. E. Hallam, S. Waring and J. R. Armstrong, *J. Chem. Soc., Faraday Trans II* **72**, 1 (1976).
[29] P. H. Turner and A. P. Cox, *J. Chem. Soc., Faraday Trans II* **74**, 533 (1978).
[30] K. Ohno, Y. Shiro and H. Murata, *Bull. Chem. Soc. Jpn* **47**, 2962 (1974).
[31] G. A. Crowder and W.-Y. Lin, *J. Molec. Struct.* **62**, 1 (1980).
[32] S. V. Trepalin, A. V. Yarkov, V. B. Sokolov and A. N. Ivanov, *Izv. Akad. Navk. SSSR, Ser. Khim.* **8**, 550 (1990).
[33] A. M. Smith and M. R. S. McCoustra, *Spectrochim. Acta* **47A**, 1661 (1991).
[34] M. R. S. McCoustra (unpublished data).