An Infrared Spectroscopic Method of Distinguishing Isomeric Disubstituted Hydrazines as Salts

By **J. A. Blair*** and **R. J. Gardner**, Chemistry Department, University of Aston in Birmingham, Gosta Green, Birmingham 4

Isomeric 1,1- and 1,2-disubstituted hydrazines may be readily distinguished by examination of the NH stretching frequencies in the i.r. spectra of their hydrochloride salts.

DISUBSTITUTED hydrazines are generally distinguished by catalytic cleavage,[1] or by their differing reactivity towards carbonyl compounds.[2] The former method is tedious and the latter may give unexpected results.[2]

Bis(organosilyl)hydrazines have been distinguished by n.m.r. spectroscopy.[3] The nitrogen-bound protons of a 1,1-disubstituted isomer are equivalent and give a singlet, but those of a 1,2-disubstituted isomer give two signals. The method is inapplicable to 1,2-disubstituted isomers with the same group on each nitrogen atom and the width and lack of fine structure [4,5] of the NH resonance reduces its general utility.

Isomeric bis(organosilyl)hydrazines may also be distinguished by examining the N–H stretching [ν(NH)] bands in the i.r. spectra of the free hydrazines.[3] Hydrazines, like amines, show strong ν(NH) bands above 3100 cm.$^{-1}$. The frequency shift between the symmetric and antisymmetric ν(NH) bands for the 1,1-disubstituted isomer is constant (76—88 cm.$^{-1}$), but the corresponding shift for the 1,2-disubstituted isomer is small (*ca.* 23 cm.$^{-1}$), and may not be observed. The method suffers from a number of drawbacks. Free hydrazines are unpleasant to handle, easily oxidized, and difficult to free from residual water. Oxidation has been shown to be responsible for discrepancies in the i.r. spectrum of a hydrazine [6] and residual water makes observation of the region above 3100 cm.$^{-1}$ difficult. More important,

---

[1] E. Fischer, *Annalen*, 1887, **239**, 248.

[2] P. A. S. Smith, 'Open-chain Nitrogen Compounds,' Benjamin, New York, 1965, vol. 2, p. 109.

[3] R. West, M. Ishikawa, and R. E. Bailey, *J. Amer. Chem. Soc.*, 1966, **88**, 4648.

[4] J. R. Crook and K. Schug, *J. Amer. Chem. Soc.*, 1964, **86**, 4271.

[5] V. S. Stopskii, V. B. Lebedev, B. V. Ioffe, and A. A. Petrov, *Doklady Akad. Nauk S.S.S.R.*, 1966, **166**, 399.

[6] A. L. Olsen and H. W. Kruse, *J. Chem. Phys.*, 1956, **24**, 1106.

however, is the fact that 1,2-dialkylhydrazines show a much larger shift than the 23 cm.$^{-1}$ observed for the bis-(organosilyl)hydrazines. For example gaseous 1,2-di*meth*ylhydrazine shows a shift of 117 cm.$^{-1}$ and solid 1,2-diphenylhydrazine a shift of 66 cm.$^{-1}$. The corresponding 1,1-disubstituted isomers show shifts of 181 and 122 cm.$^{-1}$, respectively;[7] hence spectra of both isomers must be compared before unambiguous structural assignments can be made.

Evans and Kynaston[8] developed an elegant method of determining the site of protonation of a substituted hydrazine salt. This can be extended to give a general method of distinguishing isomeric hydrazines as stable salts.

Mono-salts of 1,1-disubstituted hydrazines will have either of structures (I) and (II). The $\overset{+}{N}H$ and $\overset{+}{N}H_3$

$$R^1R^2\overset{+}{N}H{\cdot}NH_2\ X^- \qquad\qquad R^1R^2N{\cdot}\overset{+}{N}H_3\ X^-$$

(I) (II)

systems do not show strong ν(NH) bands above 3100 cm.$^{-1}$.[9] Hence structure (I) will show the typical symmetric and antisymmetric ν(NH) bands above 3100 cm.$^{-1}$, and structure (II) will show no strong bands in this region.

Mono-salts of 1,2-disubstituted hydrazines will have either of structures (IIIa) and (IIIb). The $\overset{+}{N}H_2$ system

$$R^1\overset{+}{N}H_2{\cdot}NHR^2\ X^- \qquad\qquad R^1NH{\cdot}\overset{+}{N}H_2R^2\ X^-$$

(IIIa) (IIIb)

does not absorb above 3100 cm.$^{-1}$;[9] hence each structure will show only one strong ν N–H band in this region.

1,1-Disubstituted hydrazine salts will thus show *two* or *no* ν(NH) bands and 1,2-disubstituted hydrazine salts will show *one* ν(NH) band above 3100 cm.$^{-1}$. The Table illustrates this difference.

Di-salts of 1,2-disubstituted hydrazines like structure

$$R^1\overset{+}{N}H_2{\cdot}\overset{+}{N}H_2{\cdot}R^2\ 2X^-$$

(IV)

(IV) will not show bands above 3100 cm.$^{-1}$. Structure (IV) only occurs, however, when electron-withdrawing groups are present,[8] and under these conditions the 1,2-disubstituted isomer is not likely to form a di-salt.

EXPERIMENTAL

1,2-Disubstituted hydrazines were prepared by reduction of the corresponding hydrazones with diborane.[10] I.r. spectra were determined with a Perkin-Elmer 237 spectrometer.

	ν(NH) (above 3100 cm^{-1})			Structural type
$Me_2N{\cdot}NH_2,(CO_2H)_2$	3240s		3130s	(I)
$Me_2N{\cdot}NH_2,HCl$[8]	3290s		3131s	(I)
$MeNH{\cdot}NHMe,2HCl$		—		(IV)
$Et_2N{-}NH_2,(CO_2H)_2$	3250s		3120s	(I)
$EtNH{\cdot}NHEt,HCl$[11]		3205s		(III)
$(Pr^i)_2N{\cdot}NH_2,HCl$[8]	3260s		3150s	(I)
$Pr^iNH{\cdot}NHPr^i,HCl$		3195s		(III)
$MeNH{\cdot}NH{\cdot}CH_2Ph,HCl$		3200s		(III)
$MeNH{\cdot}NH{\cdot}CH_2Ph,2HCl$		—		(IV)
$EtNH{\cdot}NH{\cdot}CH_2Ph,HCl$		3200s		(III)
$Pr^nNH{\cdot}NH{\cdot}CH_2Ph,HCl$		3200s		(III)
$Pr^iNH{\cdot}NH{\cdot}CH_2Ph,HCl$		3195s		(III)
$Bu^nNH{\cdot}NH{\cdot}CH_2Ph,HCl$		3200s		(III)
$PhCH_2(Bu^t)N{\cdot}NH_2,HCl$[12]	3320s	3230s	3170s	(I)
$Bu^tNH{\cdot}NH{\cdot}CH_2Ph,HCl$		3200s		(III)
$PhCH_2{\cdot}NH{\cdot}NH{\cdot}CH_2Ph,HCl$		3195s		(III)
$Ph_2N{\cdot}NH_2,HCl$		—*		(II)
$Pr^iCH_2(Bu^t)N{\cdot}NH_2,HCl$[13]	3220s		3120m	(I)

* Weak band at 3158 cm.$^{-1}$.[8]

[0/962 *Received, June 9th,* 1970]

---

[7] D. Hadzi, J. Jan, and A. Ocvirk, *Spectrochim. Acta*, 1969, **25***A*, 97.

[8] R. F. Evans and W. Kynaston, *J. Chem. Soc.*, 1953, 3151.

[9] C. N. R. Rao, 'Chemical Applications of Infrared Spectroscopy,' Academic Press, New York, 1963.

[10] J. A. Blair and R. J. Gardner, *J. Chem. Soc.* (*C*), 1970, 1714.

[11] R. A. Heacock and L. Marion, *Canad. J. Chem.*, 1956, **34**, 1782.

[12] C. D. Foxall, Ph.D. Thesis, University of Aston in Birmingham, 1967.

[13] J. Lakritz, Ph.D. Thesis, University of Michigan, 1960.