Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Relationship between IR C=O Frequencies of Semicarbazones and Their Solid State Structures

Vera M. Kolb [a], Timothy E. Janota [a], Cathy L. Dantzman [a], Matthew L. Kozenski [a], Dennis P. Strommen [b], James P. Snyder [c] & Greg E. Tipsword [c]

[a] Department of Chemistry, Univerity of Wisconsin-Parkside, Kenosha, WI, 53141

[b] Department of Chemistry, Carthage College, Kenosha, WI, 53141

[c] Searle Research and Development, 4901 Searle Parkway, Skokie, IL, 60077

Version of record first published: 27 Oct 2006.

To cite this article: Vera M. Kolb , Timothy E. Janota , Cathy L. Dantzman , Matthew L. Kozenski , Dennis P. Strommen , James P. Snyder & Greg E. Tipsword (1992): Relationship between IR C=O Frequencies of Semicarbazones and Their Solid State Structures, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 211:1, 403-406

To link to this article: http://dx.doi.org/10.1080/10587259208025840

Mol. Cryst. Liq. Cryst. 1992, Vol. 211, pp. 403–406
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

RELATIONSHIP BETWEEN IR C=O FREQUENCIES OF SEMICARBAZONES AND THEIR SOLID STATE STRUCTURES

VERA M. KOLB[1*], TIMOTHY E. JANOTA[1], CATHY L. DANTZMAN[1], MATTHEW L. KOZENSKI[1], DENNIS P. STROMMEN[2*], JAMES P. SNYDER[3*], AND GREG E. TIPSWORD[3]
[1]Department of Chemistry, Univerity of Wisconsin-Parkside, Kenosha, WI 53141, [2]Department of Chemistry, Carthage College, Kenosha, WI 53141, [3]Searle Research and Development, 4901 Searle Parkway, Skokie, IL 60077

(*Received July 12, 1991*)

Abstract We have recently reported numerous abnormally high IR frequencies (up to 1760 cm^{-1}) in the solid state for the carbonyl of semicarbazones (R_1R_2C=N-NH-CO-NH_2) of a series of aldehydes and ketones (Kolb et al., J. Org. Chem., 54, 2431 (1989)). We are now proposing that these high frequencies are induced by an exceptionally strong vibrational coupling of the C=O in the centrosymmetric solid-state H-bonded structure. Raman spectroscopy was used in conjunction with IR to detect this vibrational coupling. Theoretical AM1 analysis for the exceptional strength of this coupling has been performed.

Keywords: semicarbazones, IR C = O frequencies, raman C = O frequencies, AM 1 calculations, solid state of semicarbazones, vibrational coupling

INTRODUCTION

We have recently reported[1] numerous abnormally high IR frequencies (Nujol mull) for the carbonyl moiety of semicarbazones (R_1R_2C=N-NH-CO-NH_2) of a series of 86 variously substituted benzaldehydes (R_1=H, R_2=Ph), acetophenones (R_1=CH_3, R_2=Ph) and some other aldehydes and ketones. Frequencies of up to 1760 cm^{-1} were observed (cf. 1690 cm^{-1} as a normal value for the semicarbazone carbonyls, and 1640-1650 cm^{-1} for the amide and urea carbonyls). These high frequencies are the result of solid-state interactions since they shift to normal values in (DMSO) solution. X-Ray crystallographic data indicated that semicarbazones form extensive hydrogen bonded networks (Fig. 1). These very high IR C=O frequencies of semicarbazones are unprecedented for the amide-type carbonyl where amide resonance is expected and where the C=O is involved in H-bonding.

A hypothesis we set out to test in this work is that the abnormally high IR C=O frequencies are induced by the exceptionally strong vibrational coupling of the C=O in the centrosymmetric solid-state H-bonded structure (Figure 1). The high frequency IR band could be the asymmetric C=O stretch of the basic cyclic structure. The lower frequency band, the symmetric C=O stretch, should then be observed in the Raman.

This behavior has previously been observed in the well-studied case of the carboxylic acid dimers[2-4]. This proposed vibrational coupling appears to be so strong that in some cases it overrides the frequency lowering H-bonding and amide resonance effects.

In this paper we report the results of the Raman and IR studies and AM1 calculations.

EXPERIMENTAL

IR studies were done on a Perkin-Elmer 1600 FT-IR spectrometer. Raman spectra were taken on a Raman Spex spectrometer (Spex 1403 double monochromator; DMIB controller; detection by photon counting, λ_{ex} = 514.5nm). Semicarbazones are those reported in ref. 1.

RESULTS AND DISCUSSION

Selected Raman and IR data for the compounds in this study are given in Table I.

TABLE I Selected Raman and IR data for the compounds in this study.*

Compound	Raman C=O	Raman C=N	IR C=O	ΔC=O (IR-Raman)
BENZALDEHYDES (BA) SEMICARBAZONES (SC)				
BASC	1642	1613	1690	48
deuterated** BASC	1622	1614	1656	34
o-NO_2-BASC	1672	1610	1736	64
deuterated** o-NO_2-BASC	-	1609	1700	-
m-NO_2-BASC	-	1610	1722	-
p-NO_2-BASC	-	1615	1681	-
o-Cl-BASC	-	-	1732	-
m-Cl-BASC	1665	1607	1702	37
p-Cl-BASC	1655	1613	1709	54
3,4-di-OH-BASC	-	1619	1662	-
ACETOPHENONES (AP) SC				
APSC	1684	1615	1740	56
deuterated** APSC	1631	1611	1713	82
o-OCH_3-APSC	1666	1603	1694	28
m-OCH_3-APSC	-	1606	1691	-
p-OCH_3-APSC	1663	1603	1746	83
o-NO_2-APSC	1674	1607	1734	60
o-F-APSC	1671	1607	1703,1695	32
ALIPHATIC KETONES SC				
acetone SC	1669	1641	1680	11

acetone d_6 SC	1662	1641	1680	18
pinacolone SC	1663	1645	1711	48
cyclopentanone SC	1683	1651	1682	none
2-adamantanone SC	-	1649	1681	-
deuterated** 2-adamantanone SC	-	1649	1653	-
acetyl cyclohexane SC	1693	1639	1689	-

*All frequencies are in the cm^{-1}. IR data are for the Nujol mull. Raman spectra were taken in the solid state. **Deuteration occurs at both NH and NH_2 groups.

The C=N band is strong to medium intensity in Raman; it is not observed or is weak to medium in the IR. The C=O band is very weak in Raman; it is usually strong in the IR. The aliphatic ketone semicarbazones show the Raman C=N band at higher frequencies (1641-1651 cm^{-1}) than the aromatic ones (1603-1615 cm^{-1}), as expected due to the conjugation of the latter[5,6]. For the series of compounds we studied, the symmetric and asymmetric C=O stretching modes show splittings of 11-83 cm^{-1}.

To address the question of the exceptional strength of this coupling we have carried out AM1[7] semiempirical geometry optimizations for dimers and tetramers of the following planar, multiply hydrogen bonded structures (R_1=NO_2, Cl, H, CH_3, OH, NH_2 and R_2=H, Cl, H, CH_3, H, H) followed by normal coordinate analysis. In each case the carbonyl stretching frequencies are split into symmetric and asymmetric carbonyl vibrations separated by 5-22 and 13-26 cm^{-1} for the dimers (Fig. 2) and tetramers (Fig. 3) respectively. In agreement with the spectroscopic results, the lower frequencies with small transition dipoles can be classified as symmetric bands (Raman), while the higher values are asymmetric and accompanied by large transition dipoles (IR). The asymmetric stretches are consistently lower than the isolated monomer as expected for a hydrogen bonded C=O. Furthermore the AM1 data suggests the semicarbazone carbonyl frequency to be sensitive to the electronic requirements of R_1 and R_2, since the electron withdrawing groups Cl and NO_2 raise the frequency by 10-15 cm^{-1} for the tetramers relative to R=H. AM1 fails to reproduce the solid state frequency elevation effect of the asymmetric component above the monomer frequency. This can be interpreted in terms of polar solvation effects on the monomer, the inability of tetramer to model the solid state or both. Work to distinguish these possibilities is underway.

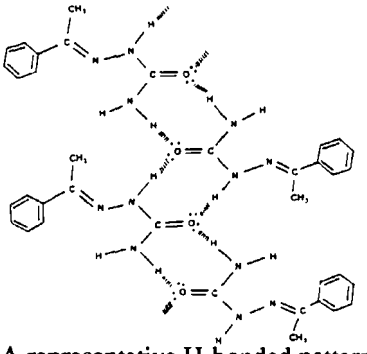

FIGURE 1 A representative H-bonded pattern for semicarbazones.

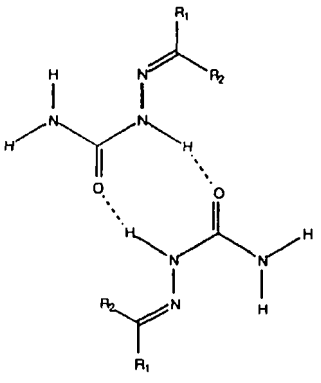

FIGURE 2 Semicarbazone dimer.

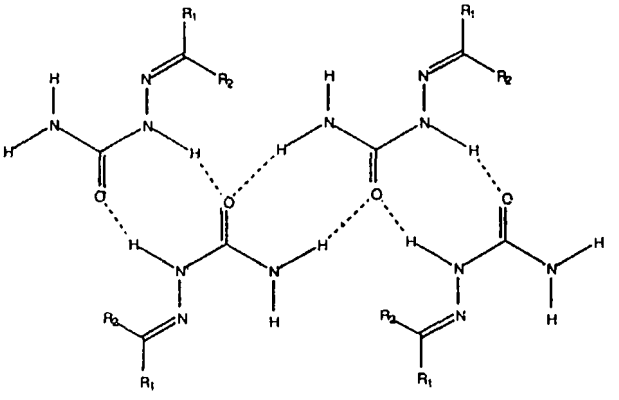

FIGURE 3 Semicarbazone tetramer.

REFERENCES

1. V.M. Kolb, J.W. Stupar, J.E. Janota, and W.L. Duax, J. Org. Chem. 54, 2341-2346 (1989) and the references cited therein.
2. N.B. Colthup, L.H. Daly, and S.E. Wiberley, Introduction to Infrared and Raman Spectroscopy, Third Ed., (Academic Press, New York, 1990), pp. 210-213, 313-314, and the references cited therein.
3. B. Schrader, Raman/Infrared Atlas of Organic Compounds, Second Ed., (VCH Publ.,New York, 1989), Section B-3.
4. J. Dybal, T.C. Cheam, and S.J. Krimm, J. Mol. Str., 159, 183-194 (1987).
5. O.A. Raevskii, R.R. Shagidullin, and Yu. P. Kitaev, Izvest. Akad. Nauk SSSR, Ser. Khim. 2, 218-222 (1966) (English translation).
6. O.A. Raevskii, R.R. Shagidullin, and Yu. P. Kitaev, Dokl. Akad. Nauk SSSR, 170, 114-117 (1966) (English translation).
7. M.J.S. Dewar, E.G. Zoebisch, E.F. Healey, and J.J.P. Stewart, J. Amer. Chem. Soc., 107, 3902-3909 (1985).