Dewar anthracenes were determined by following changes in their ¹H NMR spectra with time.

¹³C NMR Spectra. For D4: δ 15.64, 15.87, 54.84, 101.27, 129.65, 135.12, 144.05. **For D11:** δ 15.34, 15.52, 15.61, 15.96, 54.57, 54.63, 99.53, 129.70, 133.64, 134.38, 136.93, 143.99, 144.05. These spectra were measured at −60 °C. **D5** and **D6** were too short-lived to obtain ¹³C spectra.

UV Spectra. The spectrum of **D5** in Figure 1 was obtained by irradiating a solution of **5** in hexane in a quartz Dewar-UV cell at −45 °C; the spectrum was recorded at that temperature. In a similar manner, λ$_{max}$ for **D4** was at 270 nm, and for **D11** at 272 nm. **D6** was too unstable at −45 °C to obtain a UV spectrum.

Endoperoxides 18 and 19. Brief irradiation (30 min) of an undegassed solution of **13** in benzene-d_6 in an NMR tube as described in the general photolysis procedure gave endoperoxide **18**: ¹H NMR (C$_6$D$_6$) δ 1.79 (s, 3 H), 1.99 (s, 3 H), 2.07 (s, 6 H), 6.71–7.06 (m, 6 H); mass spectrum, *m/e* (relative intensity) 266 (4), 251 (9), 234 (100), 219 (36), 85 (20). In a similar manner, irradiation of **14** gave endoperoxide **19**: ¹H NMR (C$_6$D$_6$) δ 1.96 (s, 6 H), 2.09 (s, 6 H), 6.75–7.01 (m, 6 H); ¹³C NMR (C$_6$D$_6$) δ 18.56, 21.87, 81.24, 119.66, 126.91, 131.53, 131.88, 143.80 (one peak under the solvent peak); mass spectrum, *m/e* (relative intensity) 266 (4), 234 (100), 219 (32), 85 (22), 40 (16).

Irradiation of 1,4,9-Trimethylanthracene (15). Samples of **15** were irradiated in several solvents (benzene-d_6, pyridine-d_5, and chloroform-*d*) according to the general photolysis procedure. The singlet at δ 8.20 (aromatic proton at C10) in the spectrum of **15** disappeared, and new singlets appeared at δ 4.27 and 4.45 (in CDCl₃), area ratio 5:1, ascribed to the bridgehead protons in **20** and **21**, respectively. In addition, the major product **20** showed three methyl singlets approximately 0.5 ppm upfield from those in **15** (in CDCl₃, at δ 2.25, 2.39, and 2.55) whereas the minor isomer **21** showed a singlet at δ 2.50 (ratio of δ 2.39/2.50 = 5:1; the other methyl peaks for **21** were coincidental with those of **20** at δ 2.25 and 2.55; in pyridine-d_5, two of the three methyl signals for **21** were nicely resolved). The photoproducts were stable even after 3 h at 60 °C.

Abnormally High IR Frequencies for the Carbonyl Group of Semicarbazones of the Benzaldehyde and Acetophenone Series

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We have synthesized 86 semicarbazones of variously substituted benzaldehyde and acetophenone and of several other aldehydes and ketones for comparison. The IR data in Nujol mull revealed numerous abnormally high frequencies for the carbonyl of semicarbazones of up to ca. 1760 cm⁻¹ (cf. 1690 cm⁻¹ as a normal value for semicarbazones carbonyls and 1640–1650 cm⁻¹ for the amide and urea carbonyls). These high C=O frequencies shift to normal values in DMSO solution. The origin of the high C=O frequencies could not be ascribed to the stereoelectronic effects of the substituents on the aromatic ring. It appeared that the high C=O frequencies are caused by the solid-state structure. The X-ray structural determination of two semicarbazones indicated a network of H-bonds in which each C=O is involved in a bifurcated H-bond with NH₂ and NH from two different molecules. The solution and solid-state ¹³C NMR studies of semicarbazones are also described.

Introduction

Semicarbazones **I** are very common derivatives of aldehydes and ketones and are frequently used in the qualitative organic analysis of these carbonyl compounds.[1,2]
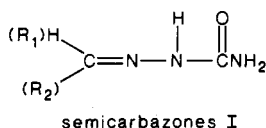
semicarbazones I

The IR frequencies of the carbonyl group of the semicarbazones drew interest rather early. Wang[3] observed that the IR frequency of the carbonyls of the semicarbazones is normally found at ca. 1690 cm⁻¹ (in KBr), which appeared abnormally high as compared to those of amides **II** and ureas **III** at 1640–1650 cm⁻¹.

amides II   ureas III
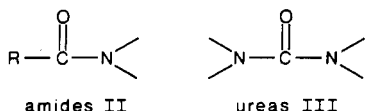
Wang attempted to explain the shift to higher frequencies of **I** vs **III** by the inductive effect of the extra nitrogen in **I**: The combined inductive effects would pull
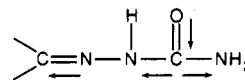
the π cloud of carbonyl closer to the carbon, diminishing the polar character of the C=O. This would cause a rise in the IR frequency of the C=O.

We were astonished to find during a routine organic qualitative analysis laboratory experiment that *o*-nitrobenzaldehyde semicarbazone exhibits an abnormally high C=O frequency at 1737 cm⁻¹ (in Nujol mull). A literature search revealed that some isolated cases of the abnormally high C=O frequencies of semicarbazones were observed earlier. Thus, Davison and Christie[4] report 1745 cm⁻¹ for

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(1) Rappoport, Z. *CRC Handbook of Tables for Organic Compound Indentification*, 3rd ed.; CRC Press: Boca Raton, FL, 1984.
(2) Shriner, R. L.; Fuson, R. C.; Curtin, D. Y.; Morrill, T. C. *The Systematic Identification of Organic Compounds*, 6th ed.; J. Wiley and Sons: New York, 1980.
(3) Wang, T. S. *Appl. Spectrosc.* 1968, *22*, 167–169.

o-nitrobenzaldehyde semicarbazone and 1750 cm^{-1} for acetophenone semicarbazone. These authors also observed several C=O frequencies in the range of 1720 cm^{-1} for the semicarbazones of some aliphatic aldehydes and ketones. They made a remark that "The marked shifts of ν (C=O) in the aromatic derivatives merit further study by means of a series of substituted benzaldehyde and acetophenone derivatives; the shifts should be related to Hammett's σ functions". However, no follow-up was reported.

Thus, we decided to synthesize a series of semicarbazones of benzaldehyde and acetophenone with ortho, meta, and para substituents of various electronic properties and look at the IR frequencies for the C=O of these semicarbazones. Our objectives were to first establish if the observed abnormally high frequencies are rare exceptions or more common occurrence and then to study the origins of these high frequencies.

Experimental Section

Melting points were taken on a Mel-Temp apparatus and are not corrected. The IR spectra were taken on a Perkin-Elmer Model 1320 spectrophotometer. The IR diffuse reflectance studies were done at the research division of Nicolet Company (by S. R. Lowry and K. Kempfert). The ^{13}C and ^{1}H NMR spectra were taken on a Bruker 360-MHz instrument (at the University of Wisconsin—Madison) (by B. R. Adams) and a JEOL Model PMX-60 instrument, respectively. Solid-state ^{13}C NMR spectra were recorded on a Chemagnetics Model CMS-300 (at the University of Wisconsin—Madison) (by Dr. T. W. Root). Most of the ketones used in this study were obtained from Aldrich Chemical Co., few were obtained from Fluka, and some were synthesized according to published procedures.

The IR spectra of semicarbazones were taken in Nujol mull. Some were taken in DMSO. Concentrated solutions of substances in DMSO were obtained by grinding the solid with DMSO in the mortar, quickly filtering the suspension, and placing the liquid in the cell.

The semicarbazones were synthesized by the procedure from ref 2, p 179, and were recrystallized from EtOH or EtOH–H$_2$O, until constant melting point.

Deuteration of semicarbazones was achieved by recrystallization from hot D$_2$O or DMSO (small amount)–D$_2$O.

Results and Discussion

We have synthesized 86 semicarbazones (SC) of variously substituted benzaldehyde (BA), acetophenone (AP), and of several other aldehydes and ketones for comparison. The IR spectral data for these semicarbazones are presented in Tables I and II (for aldehydes and ketones, respectively), together with the IR spectral data on starting materials and melting points of semicarbazones.

The Nujol mull IR spectra of all of the semicarbazones studied (Tables I and II) can be divided into four different categories in respect to the number of bands between ca. 1650 and 1750 cm^{-1}: one abnormally high band, one abnormally high and one normal band, one normal band, and two normal bands. A band higher than 1700 cm^{-1} was considered high, and one below 1700 cm^{-1} was considered normal. These different categories probably reflect the complexity of the C=O absorption, which is like an amide I type band. The second band could be related to the amide II band. However, for simplicity and in line with Wang's nomenclature,[3] we shall refer to the highest band as that of C=O.

In DMSO solution all the semicarbazones studied had their C=O frequency shifted to the normal range of ca. 1695 cm^{-1}. In addition, only one peak was seen in cases where two would be observed in a Nujol mull.

The inspection of IR data on semicarbazones in Nujol from Tables I and II reveals numerous abnormally high frequencies for their carbonyls. In the Nujol mull frequencies of up to ca. 1760 cm^{-1} were observed (cf. 1690 cm^{-1} as a normal value, ref 3). The diffuse reflectance IR spectra were taken on selected samples and were essentially identical with the Nujol data. The diffuse reflectance spectra are taken in a loose KBr powder. These studies indicate the absence of some unusual interactions in the Nujol, which could be responsible for the observed high IR frequencies.

A possible relationship between these high frequencies and the electronic properties of the substituents on the benzene ring is not obvious, as shown by the following selected values from Tables I and II for the carbonyl frequencies. BA-SC, 1690 cm^{-1}. Substituted BA-SC, *o*, *m*, and *p*, respectively: NO$_2$ 1737, 1722, 1682; F 1690, 1738, 1715; Cl 1736, 1700, 1705; Br 1725, 1705, 1705; CH$_3$ 1695, 1686, 1710 cm^{-1}. AP-SC, 1741 cm^{-1}. Substituted AP-SC, *o*, *m*, and *p*, respectively: NO$_2$ 1728, 1728, 1678; F 1693, 1717, 1743; Cl 1729, 1709, 1720; Br 1730, 1708, 1712; CH$_3$ 1685, 1702, 1690 cm^{-1}.

In order to elucidate the origins of these high frequencies for the C=O of semicarbazones in Tables I and II, we undertook the following studies.

First, we were interested in finding out about the configurational purity of our compounds. The inspection of the molecular models reveals that syn (I′) isomers would be sterically more crowded than the anti (II′) isomers.

syn (I′)   anti (II′)
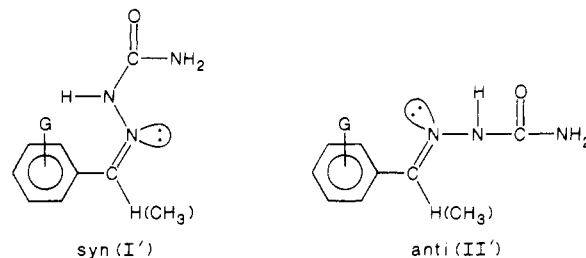
Our ^{13}C NMR study revealed the existence of a single isomer in all cases studied.[5] Namely, only one peak per carbon was observed, corresponding to a single, presumably anti isomer. Two isomers, syn and anti, would show two distinct sets of peaks.[6-8] Also the cyclic triazoline form (III′), in which the C=O group would be expected to ab-

III′
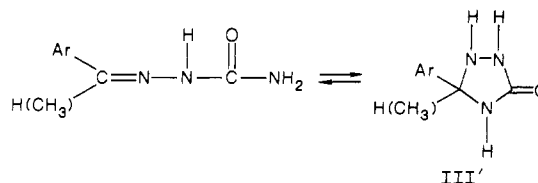
sorb at high IR frequencies,[9,10] was not observed (it would give a different set of peaks), in agreement with the literature findings.[11] The form III′ was not observed in the

(4) Davison, W. H. T.; Christie, P. E. *J. Chem. Soc.* **1955**, 3389–3391.

(5) Adams, B. R.; Root, T. W.; Darling, S. D.; Kolb, V. M. Third Chemical Congress of North America, Toronto, Canada, June 5–10, 1988, Abstract ORG-67. Also see a related abstract, ORG-409.

(6) Bunnell, C. A.; Fuchs, P. L. *J. Org. Chem.* **1977**, *42*, 2614–2617.

(7) Naulet, N.; Filleux, M. L; Martin, G. J.; Pornet, *J. Org. Magn. Reson.* **1975**, *7*, 326–330.

(8) Hawkes, G. E.; Herwig, K.; Roberts, J. D. *J. Org. Chem.* **1974**, *39*, 1017–1028.

(9) Nakanishi, K.; Solomon, P. H. *Infrared Absorption Spectroscopy*, 2nd ed.; Holden-Day Inc.: San Francisco, 1977; p 43.

(10) Bellamy, L. J. *Advances in Infrared Group Frequencies*; Methuen and Co., Ltd.: London, 1968; pp 132–135.

(11) Uda, M.; Kubota, S. *J. Heterocycl. Chem.* **1978**, *15*, 807–812.

Table I. IR and Other Data for a Series of Semicarbazones of Benzaldehyde and Some Other Aldehydes

| | aldehyde | | corresponding semicarbazone | |
| | | | IR C=O (cm⁻¹) | |
name	IR[a] C=O (cm⁻¹)	mp (EtOH), °C (lit. mp, °C)[b]	Nujol mull	DMSO soln
benzaldehyde (BA)	1696, 1650 (neat)	223–226 (222)	1690, 1650	1698
o-NO₂-BA	1708	248–250 (256)	1740	
m-NO₂-BA	1705, 1690	239–241 (246)	1722, 1660	
p-NO₂-BA	1705, 1685	210–214 (221)	1682, 1632	
o-F-BA	1700 (neat)	231–232	1690	1697
m-F-BA	1705 (neat)	218.5–220 (212)	1738, 1675	1697
p-F-BA	1700 (neat)	225–226.5 (216)	1715, 1670	1694
o-Cl-BA	1700 (neat)	226–230 (225)	1725, 1656	1698
m-Cl-BA	1702 (neat)	228–231 (228)	1700	
p-Cl-BA	1710	228–232 (230)	1705, 1662	1698
o-Br-BA	1696, 1645 (neat)	215–218 (214)	1725, 1655	1698
m-Br-BA	1705 (neat)	227–229 (205)	1705	
p-Br-BA	1685	225–229 (228)	1705, 1668	
o-I-BA	1692	208–210 (206)	1703	
p-I-BA	1710, 1690	234.5–236 (224)	1708, 1669	
o-CH₃-BA	1726, 1695 (neat)	206–209 (208)	1700	
m-CH₃-BA	1703 (neat)	211–215 (213)	1687, 1639	
p-CH₃-BA	1700, 1690 (neat)	214–217 (221)	1708, 1665	1698
o-OH-BA	1667, 1648 (neat)	230–231	1697	
m-OH-BA	1669	191–194 (198, 199)	1667	
p-OH-BA	1668	218.5–221 (224, 280)	1684	
o-OCH₃-BA	1691, 1669	213–216 (215)	1717, 1693	
m-OCH₃-BA	1705, 1688	209–210 (233)	1688, 1645	1696
p-OCH₃-BA	1690	209.5–212 (210, 203)	1689, 1647	1692
2,6-di-NO₂-BA	1710	220.5–222	1702	
2,4-di-Cl-BA	1694, 1682	251.5–254	1731, 1662	
2,6-di-Cl-BA	1699	220–222.5	1732, 1665	
2,3,6-tri-Cl-BA	1705	229–232	1741, 1665	
2,3,5-tri-Cl-BA	1694	251–253	1739, 1666	
2,6-di-F-BA	1708	238–239	1696	
2,4-di-F-BA	1699	251–253	1751, 1698, 1762, 1720	
o-NH₂-BA	1672	197–200	1688	
p-N,N-di-CH₃-BA	1675, 1661	224–225.5 (222)	1691, 1646	
3,4-di-OH-BA	1655	210–240 (230)	1667	
3,4,5-tri-OH-BA		230 dec	1691	
3,5-di-t-Bu-4-OH-BA	1670	227–229	1684	
4-OH-3-OCH₃-BA	1669	236–237.5 (230, 240)		
2-CF₃-BA	1705 (neat)	232.5–235	1706	
penta-F-BA	1715, 1653 (neat)	251–252	1762, 1724	
mesityl aldehyde	1688 (neat)	193–195 (188)	1705, 1675	
1-naphthaldehyde	1689 (neat)	226–228 (221)	1728, 1688	
2-naphthaldehyde	1697	249.5–251 (245)	1699	
2-pyridinecarboxaldehyde	1712 (neat)	191–192.5	1692	
3-pyridinecarboxaldehyde	1705, 1667	218–219.5 (217–218.5 for D analogue)	1691, 1666	
4-pyridinecarboxaldehyde	1713, 1673	207–210	1702	
2-pyrrolecarboxaldehyde	1725, 1657	179–181.5 (183.5)	1652, 1635	1687, 1691 in dioxane
2-furaldehyde	1682 (neat)	200–201.5 (202)	1689, 1656	
3-furaldehyde	1685 (neat)	214–215 (211)	1688, 1653	
4-Ph-BA	1709, 1697, 1683	244.5–246.5 (243 dec)	1749	

[a] In Nujol mull unless otherwise noted. The highest band is the C=O. Another band in the region of 1650–1700 cm⁻¹, which is sometimes observed, is also listed for a comparison with the region of the second band for semicarbazones. [b] Reference 1.

^{1}H NMR spectrum either. The aldehyde H in the chain form resonates at 7.5–8.00 ppm, but in the cyclic form it appears at 5.0–6.0 ppm.[11] The latter absorption has not been observed.

Next, an attempt was made to correlate the high carbonyl frequencies in the IR with the ^{13}C NMR shifts in solution. In DMSO-d_6 solution the C=O shifts were found to be essentially the same for the semicarbazones with the abnormally high and normal carbonyl IR frequencies.[5] Table III shows the ^{13}C NMR shifts for various semicarbazones, whose IR C=O frequencies vary. In all cases studied so far, one finds essentially the same C=O shift of 156–157 ppm, which is also the expected value from the literature.[12] The chemical shifts for the carbonyl or any other carbon were not sensitive to dilution.

The above findings prompted a solution IR study, which showed a shift of high carbonyl to the normal values of ca. 1700 cm⁻¹ in DMSO (Tables I and II) (DMSO was chosen since the semicarbazones studied were virtually insoluble in other solvents that would be more suitable for IR studies). Thus, it appeared that the high carbonyls may be due to the solid-state conformation/environment.

The origin of the high IR C=O frequency in the solid state could be linked to a specific combination of the resonance and inductive effects and the intermolecular H-bonding, but only with difficulty and without any predictive value. Thus, we decided to explore the following possibility.

It has been reported in the literature[13] that a substantial shift toward higher frequency occurs in α-halo ketones in

(12) Levy, G. C.; Lichter, R. L.; Nelson, G. L. *Carbon-13 Nuclear Magnetic Resonance Spectroscopy*, 2nd ed.; J. Wiley and Sons: New York, 1980; p 163.

(13) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1975; Vol. I, pp 157–159, and the references cited therein.

Table II. IR and Other Data for a Series of Semicarbazones of Acetophenone and Some Other Ketones

ketone			corresponding semicarbazone	
			IR C=O cm⁻¹	
name	IR C=O (cm⁻¹)	mp (EtOH), °C (lit. mp, °C)[b]	Nujol mull	DMSO soln
acetophenone (AP)	1685 (neat)	198–200 (198–199; 203)	1738	1698
o-NO₂-AP	1705 (neat)	210–213 (210)	1728	
m-NO₂-AP	1688	263–264 (257)	1728	
p-NO₂-AP	1688	245–248	1678	
o-F-AP	1691 (neat)	193–195	1693	
m-F-AP	1688 (neat)	213–215	1717, 1689	
p-F-AP	1688 (neat)	209–212 (219)	1743, 1684	
o-Cl-AP	1694 (neat)	180–181 (160)	1729, 1678	
m-Cl-AP	1685 (neat)	263–238 (232)	1709	
p-Cl-AP	1685 (neat)	201–202 (204)	1720, 1685	
o-Br-AP	1700 (neat)	172–174 (177)	1730, 1675	
m-Br-AP	1687 (neat)	235–236 (233)	1708	
p-Br-AP	1672	209–210 (208)	1712, 1680	
o-CH₃-AP	1680 (neat)	206–208 (210, 205)	1685, 1660	
m-CH₃-AP	1680 (neat)	202–204 (203, 198)	1702	
p-CH₃-AP	1685 (neat)	203–204 (204–205)	1690	
o-OH-AP	1642, 1618 (neat)	220–221 (210)	1707	
m-OH-AP	1662	192–194 (189–191)	1681	
p-OH-AP	1663	200.5–202 (199)	1683	
o-OCH₃-AP	1675 (neat)	181–183.5 (183)	1692	
m-OCH₃-AP	1682 (neat)	194–195 (196)	1692	
p-OCH₃-AP	1684	197–199.5 (197–198)	1750, 1702	1697
2',3',4'-tri-Cl-AP	1689	224–226.5	1762, 1678	1702
2',3',4',5',6'-penta-F-AP	1715, 1650 (neat)	235–236.5	1764, 1662	
methyl cyclohexyl ketone	1710 (neat)	174–175 (177)	1688, 1660	
pinacolone	1709 (neat)	157.5–159 (157–158)	1711, 1643	
cyclopentanone	1746 (neat)	214–216 (210; 216–217)	1678, 1650	
cyclohexanone	1714 (neat)	(166–167)	1670	
(+)-camphor	1745	238.5–244.5 (236–237)	1698, 1663	
2-adamantanone	1722	290–294	1680, 1653	
propiophenone	1688 (neat)	178.5–181 (173–174, 182)	1714, 1678	
butyrophenone	1687 (neat)	191–193 (187–188, 191)	1678	1695
2-acetylpyridine	1699 (neat)	202–204.5	1688, 1678	
3-acetylpyridine	1689 (neat)	209–211.5	1697, 1683, 1663	
4-acetylpyridine	1696 (neat)	198–205	1681	
2-acetylfuran	1678 (neat)	144.5–146.5 (150)	1695	
2-acetylpyrrole	1645	185–189	1674	
1-acetylnaphthalene	1678 (neat)	226–230 (222.5–224)	1727, 1695, 1678	
4-acetylbiphenyl	1682	246.5–248.5	1758	

[a] In Nujol mull unless otherwise noted. The highest band is the C=O. Another band in the region of 1650–1700 cm⁻¹, which is sometimes observed, is also listed for a comparison with the region of the second band for semicarbazones. [b] Reference 1.

Table III. ¹³C NMR Chemical Shifts for the C=O and C=N Carbons of Some Semicarbazones from Tables I and II

| compound	¹³C NMR (in DMSO-d₆) (ppm) C=O	C=N	IR ν(C=O) (cm⁻¹) (from Tables I and II)
benzaldehyde semicarbazone	156.7	139.2	1690
o-tolualdehyde semicarbazone	156.6	139.7	1695
o-nitrobenzaldehyde semicarbazone	156.3	147.7	1737
o-fluorobenzaldehyde semicarbazone	156.5	131.7	1690
m-fluorobenzaldehyde semicarbazone	156.6	137.7	1738
acetophenone semicarbazone	157.2	143.9	1741
o-chloroacetophenone semicarbazone	157.0	144.8	1743
mesityl aldehyde semicarbazone	156.6	139.7	1705

which Cl is eclipsed with C=O. The effect is not observed if Cl is staggered with C=O:

The high frequency C=O shift was ascribed to a field effect. Oxygen and nitrogen atoms at the same point as

halogen behave similarly.[13]

It is possible that the N lone pair of the C=N of the semicarbazones is in the eclipsed position with the C=O and causes a similar field effect as halogen:
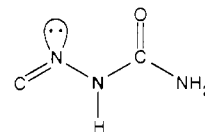
Such a conformation, or the cyclic triazoline III' (vide supra), may occur in the solid state, but may not necessarily be found in the solution where the molecule has more degrees of the conformational freedom. Also, DMSO may disrupt the internal H-bonded structure of the crystal or change the equilibrium position between the chain and ring form III'.

Thus we decided to perform solid-state ¹³C NMR and the X-ray crystallographic studies of our molecules, in order to learn about their solid-state conformations and the environment of the C=O group.

¹³C solid-state NMR spectra were collected at 75 MHz by using cross-polarization and "magic-angle" spinning on a Chemagnetics CMC-300 A spectrometer.[5] With spinning speeds of 2000–3600 Hz, isotropic shifts could be identified for all carbon atoms in the semicarbazones and were found in the solid state to differ slightly from the values determined in solution. Shifts were found to vary slightly for
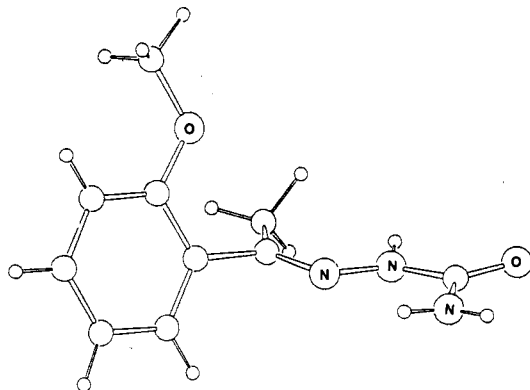
Figure 1. View of *o*-methoxyacetophenone semicarbazone.

different semicarbazones and were in the range of 120–135 ppm for ring carbons, 145–150 ppm for C=N carbons, and 155–160 ppm for the carbonyl carbons. The latter two peaks were broadened by dipole–dipole coupling to neighboring ^{14}N quadrupolar nuclei. These C=O peaks did not look substantially different for benzaldehyde semicarbazone, which exhibits normal C=O in the IR, and the *o*-nitro analogue, which exhibits abnormally high C=O in the IR. Work is underway to reconstruct the full chemical shielding tensors with the C=N and C=O carbons, but is hindered by the interactions with adjacent quadrupole moments.

The literature search revealed that no X-ray structures of semicarbazones were reported. We have submitted more than 30 semicarbazones from Tables I and II for the X-ray structural determination. Very few were found to have suitable crystals. The crystal structure of *o*-methoxyacetophenone semicarbazone was solved, and that of acetophenone semicarbazone was solved only partially.[14] The complete X-ray data will be published separately by W. L. Duax. We present here some qualitative data.

Figure 1 represents a view of *o*-methoxyacetophenone semicarbazone, which shows a normal C=O frequency (1685 cm^{-1}). The semicarbazone is found in an open-chain form. There is no eclipsing of the N lone pair of the C=N with the C=O. The C=N is not in the same plane as the benzene ring.

A very similar structure was revealed for acetophenone semicarbazone, which shows an abnormally high C=O frequency (1739 cm^{-1}), except that the C=N was in the plane of the benzene ring. The benzene ring caused a disorder, which prevented a complete structure determination.

However, the most striking feature of both X-ray structures was the complex pattern of H-bonding, which was qualitatively the same in both cases. The C=O group is involved in a bifurcated H-bonding with the NH₂ and NH of two other semicarbazone molecules (Figure 2). Only one H of NH₂ is involved in H-bonding with C=O; the other H may possibly interact with the N lone pair of the C=N.

It was very interesting to find that the abnormally high C=O of acetophenone semicarbazone is actually H-bonded via both of its oxygen lone pairs. The hydrogen bonding usually shifts the C=O frequency to lower values.

When the NH₂ and NH groups of semicarbazones were deuterated, the carbonyl frequencies of these compounds were ca. 30 cm^{-1} lower than those of nondeuterated compounds (Table IV). The carbonyl group that is involved
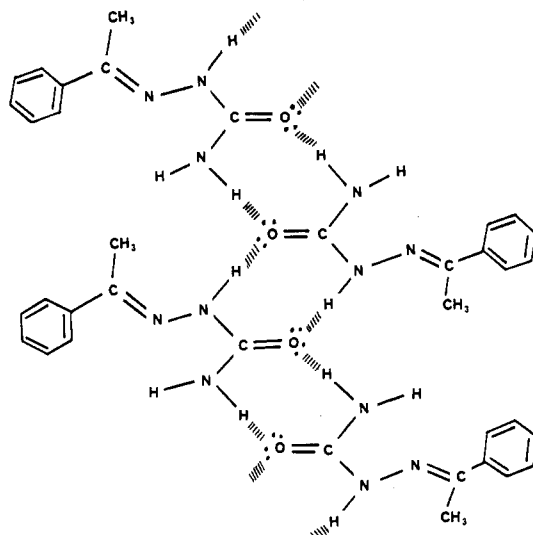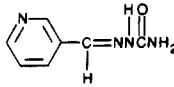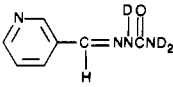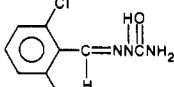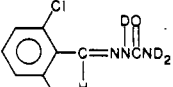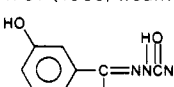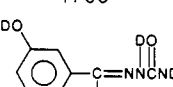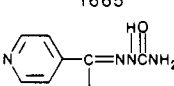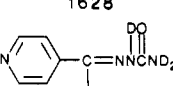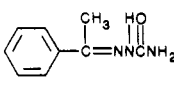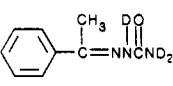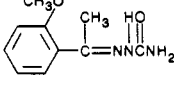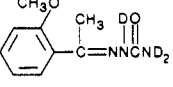

Figure 2. Hydrogen bonding in acetophenone semicarbazone.

Table IV. IR Data for Deuterated Compounds

in hydrogen bonding should have a lower frequency, since hydrogen is a better H-bond donor than D.[15] However, the opposite was found.

In Krimm and Bandekar's recent studies on IR spectra of polypeptides,[16] it was shown that the amide I band observed (which would be related to what we term the C=O band) is predominately a C=O stretch plus a CN stretch, but it can also contain a significant contribution from an NH in-plane bending. The presence of the latter

(14) Kolb, V. M.; Janota, T. E.; Stupar, J.; Duax, W. L. International Symposium on the Electronic Structure and Properties of Molecules and Crystals, Cavtat, Yugoslavia, Aug. 29–Sept. 3, 1988, Abstract p 204.

(15) Halevi, E. A. In *Progress in Physical Organic Chemistry*; Cohen, S. G., Streitwieser, A., Taft, R. W., Eds.; Interscience Publ.: New York, 1963; Vol. I, pp 119–123.

(16) Krimm, S.; Bandekar, J. In *Advances in Protein Chemistry*; Anfinsen, C. B., Edsall, J. T., Richards, F. M., Eds.; Academic Press: New York, 1986; Vol. 38, pp 181–364, and the references cited therein.

is mainly responsible for the downshift in the amide I frequency on N-deuteration.[16] It is felt that an analogous process occurs in our deuteration studies of semicarbazones.

In conclusion, we have established the following. The IR frequencies for the carbonyl group of semicarbazones of variously substituted benzaldehydes and acetophenones often fall in an abnormally high frequency range. The origin of the high C=O frequencies could not be ascribed to the electronic effects of the substituents.[17] The high frequencies shift to normal values in the DMSO solution. This high C=O frequency phenomenon seems to be related to the solid-state structure of semicarbazones. The X-ray structures of two semicarbazones indicated a network of H-bonds in which each C=O is involved in a bifurcated bond with NH_2 and NH from two different molecules. If one assumes that other semicarbazones would form similar H-bond patterns, it is possible that the H-bonding in the solid state could be related to the observed carbonyl frequencies. The carbonyls of semicarbazones exhibit complex bands, which include NH bends. The H-bonding in the solid state could cause the N–H bend component to shift the higher band, the "C=O" one, toward higher frequencies. Theoretical studies of such systems are needed.

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(17) It is interesting that a plot of $\nu_1-\nu_0$ in the solid state vs Hammett σ constants for the substituents in the ring gives a straight line.[14] A best fit was found when $\sigma > 0$. For para-substituted semicarbazones, the more positive σ, the lower the C=O. For meta-substituted semicarbazones, the greater σ, the higher the C=O.

Effect of Silica Gel on the Benzenesulfinic Acid Catalyzed Isomerization of Vinylsilanes. Formation of Silyl Benzenesulfinate

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A new method for the isomerization of (Z)-vinylsilanes into the E isomers has been developed. In contrast to the facile protodesilylation of vinylsilanes with arenesulfinic acids, use of silica gel as an additive in the reaction of vinylsilanes with benzenesulfinic acid makes possible the selective isomerization of the double-bond geometry by decreasing the rate of the competing protodesilylation. On the basis of the finding that the isomerization proceeds on the surface of the silica gel activated with benzenesulfinic acid and that benzenesulfinic esters such as ethyl, tributylstannyl, and trimethylsilyl benzenesulfinates are also effective as catalysts for the isomerization, the selective isomerization of vinylsilanes was interpreted in terms of the in situ formation of silyl benzenesulfinate bound to a silanol group of the surface of silica gel.

The strong β-effect of trialkylsilyl groups makes possible the use of vinylsilanes as the most important vinyl anion equivalent species in modern organic synthesis.[1] Vinylsilanes react with a variety of electrophiles including halogens, acid chlorides, acetals, sulfenyl chlorides, and immonium salts in a stereo- and regiospecific manner, yielding substitution products.

Recently, Büchi and Wüest reported that catalytic p-toluenesulfinic acid in wet refluxing acetonitrile is a reagent of choice for the protodesilylation of vinylsilanes, especially when acid-sensitive groups are present in the compound. Interestingly, the p-toluenesulfinic acid promoted cleavage of vinylsilanes lacks stereospecificity. Both E and Z isomers of 1-(trimethylsilyl)octene gave the same stereoisomeric mixture of deuterated olefins when cleaved with deuterio-p-toluenesulfinic acid (Scheme I).[2]

However, protodesilylation of vinylsilanes in the presence of strong acids such as hydriodic, hydrochloric, hydrobromic, and trifluoromethanesulfonic acids as well as weak acids such as acetic acid has been shown to proceed in a highly stereospecific manner with retention of configuration of double bonds.[3] To rationalize the retention

Scheme I

Scheme II
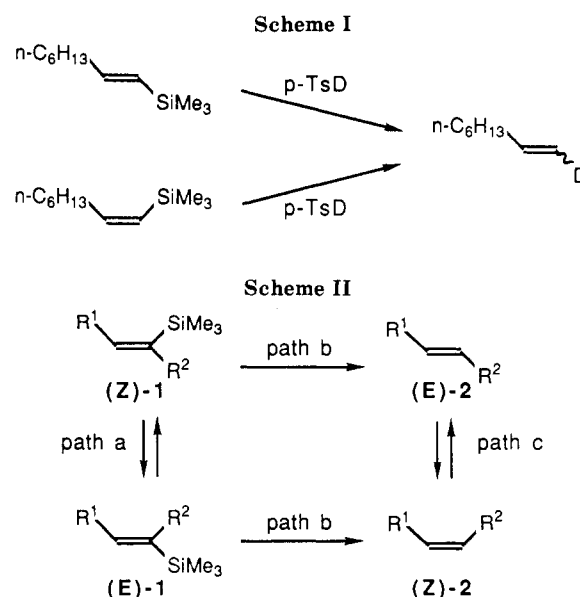
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of the alkene geometry on protodesilylation using protic acids, Koenig and Weber proposed that simultaneously