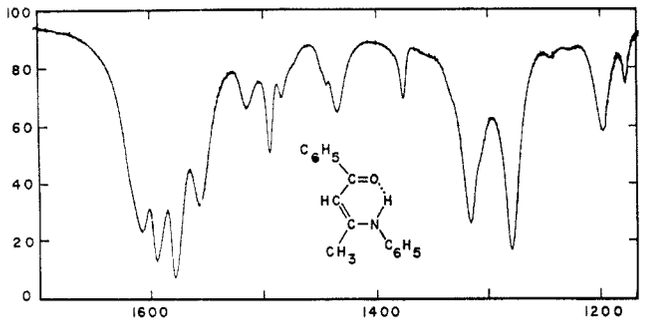


Figure 1.—The infrared spectrum of 3-(N-methylamino)crotonophenone (CCl_4 solution).

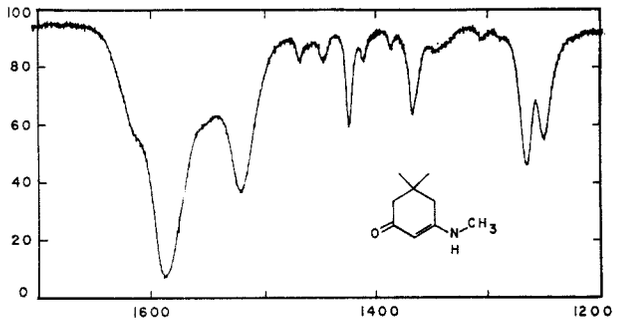


Figure 2.—The infrared spectrum of 3-(N-methylamino)-5,5-dimethylcyclohexen-1-one ($CDCl_3$ solution).

and the results provide an estimate of the vibrational coupling in these ketamines.

The spectra (Figure 1) of the Schiff base, 3-(N-methylamino)crotonophenone (I) indicate that the majority of the bands are shifted by several reciprocal centimeters; therefore, extensive coupling is present. If extensive coupling were not present, the N–H frequency would shift by 8 or more cm^{-1} and the carbonyl and double-bond frequencies would shift only slightly upon N^{15} substitution.[3] (See Table I.)

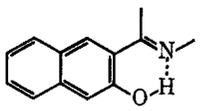
TABLE I

INFRARED BAND POSITIONS FOR 3-(N-METHYLAMINO)CROTONOPHENONE (CCl_4 SOLUTION)

N^{14} position, cm^{-1}	N^{15} shift, cm^{-1}	N^{14} position, cm^{-1}	N^{15} shift, cm^{-1}
1609	−3	1435	−2
1596	−3	1376	0
1579	−3	1317	−2
1558	−2	1281	−4
1495	0	1198	0

Since the ring system in 3-(N-methylamino)-5,5-dimethyl-2-cyclohexen-1-one (II, Figure 2) prevents intramolecular association, this compound is a useful model for comparison. The infrared band at 1586 cm^{-1} (the amide I)[1,2] shifts by 1 cm^{-1} upon N^{15} substitution,[7] while the amide II band at 1519 cm^{-1} shifts by 14 cm^{-1} and the 1266-cm^{-1} amide III band shifts by 3 cm^{-1}. Since the amide I band is usually considered to be largely a C=O stretching mode, the amide II a N–H scissor vibration and the amide III a N–H stretching frequency,[1] the results obtained here are not unexpected.

The Schiff base 3-(N-methylacetimidoyl)-2-naphthol (III) contains a hydrogen bonded C=N and O–H linkage. The results again are consistent with the concept of group frequencies. There is an appreciable isotopic shift of 18 cm^{-1} in the C=N stretch (at 1630



cm^{-1}). The 1331- and 1302-cm^{-1} bands shifting 1 cm^{-1} and a broad band at 1065 cm^{-1} shifting 6 cm^{-1} are the other nitrogen sensitive frequencies. Broad bands at 1526, 1445, and 1213 cm^{-1} are not noticeably affected by isotopic substitution of the nitrogen.

By comparison with the spectra of II and III, the strong coupling observed with I is a result of both hydrogen-bond chelation and the near equality of the double band and carbonyl frequencies.

Experimental Section

The infrared spectra were taken on a Cary White Model 90 infrared spectrometer. The band width was set to 2 cm^{-1} or less and the spectra were run in triplicate and averaged. The three determinations agreed within 1 cm^{-1}. The solvents used were either carbon tetrachloride or deuteriochloroform. The compounds have been described in earlier reports.[6]

Registry No.—3-(N-Methylamino)crotonophenone, 7721-58-6; 3-(N-methylamino)-5,5-dimethylcyclohexen-1-one, 701-58-6; III, 7721-60-0.

The Proton Magnetic Resonance Spectra of Thiocarboxamides

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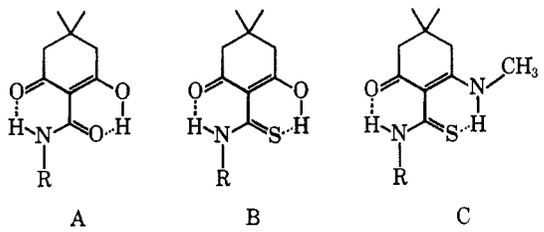
The β-diketamide group common to N-substituted 2-carbamoyldimedone derivatives (A) is an unusual cross-conjugated system.[1] Proton magnetic resonance (pmr) spectra indicate that the compounds are enolic and that the enolic and the amino hydrogens are involved in *strong* hydrogen bonding as evidenced by the large downfield chemical shifts of these protons. The chemical shift of the enolic proton of $\delta = 18$ ppm implies that the hydrogen bond in this system is stronger than the one in enols such as acetylacetone ($\delta = 16$ ppm).[2]



A B C

(1) G. Dudek and G. P. Volpp, *J. Org. Chem.*, **30**, 50 (1965).
(2) G. Dudek, *ibid.*, **30**, 548 (1965).

(7) The frequency given is always the one for the N^{14} compound.

Recently Goerdeler and Keuser[3] reported the synthesis of the sulfur analogs of the carbamoyldimedones (dimedone = 5,5-dimethylcyclohexane-1,3-dione). These compounds (B) are readily obtained by treating a β-diketone, such as dimedone, with an isothiocyanate. Since the ability of sulfur to hydrogen bond is a topic of current interest,[4,5] several compounds of type B have been synthesized and their pmr spectra have been determined (Table I).

TABLE I

PROTON MAGNETIC RESONANCE DATA FOR THE CARBOXAMIDES

Compound[a]	Solvent	R, J[b]	NH[c]	OH[c]
B	$CDCl_3$	C_6H_5	13.97	17.37
	CCl_4	C_2H_5 5.0, 7.2	12.2	17.08
	$CDCl_3$	C_2H_5 5.0, 7.2	12.3	17.17
	CCl_4	CH_3 4.8	12.2	17.06
	$CDCl_3$	CH_3 4.85	12.3	17.11
A[d]	$CDCl_3$	C_6H_5	11.7	17.9
	CCl_4	CH_3 5.1	9.6	18.15
	$CDCl_3$	CH_3 5.2	9.7	18.13
C	$CDCl_3$	C_6H_5 5.15[e]	14.2, 14.7	

[a] Since the nomenclature for these compounds is awkward, the letter refers to the figures in the text. [b] J in hertz. [c] In parts per million from tetramethylsilane. [d] Data taken from ref 1. [e] Coupling to methyl.

The data in Table I indicate that substitution of sulfur for the amide oxygen does not greatly alter the nature of the conjugated system. The hydrogen bonds involving the NH are somewhat stronger in the sulfur compounds (B) while the oxygen–sulfur–hydrogen bridges are slightly weaker than in the oxygen derivatives (A). The splitting of 5 Hz resulting from the coupling of the NH to the adjacent methyl (or ethyl) locates the proton on nitrogen with little exchange to the oxygen. Upon lowering the temperature of a chloroform solution of N-methyl-2-thiocarbamoyldimedone (B, R = CH_3) to $-40°$, little change in the pmr spectrum was observed.

An interesting member of the series is formed when the enolic hydroxyl is replaced by a methylamino group as in compound C. The pmr spectra indicate that both NH groups are strongly chelated, but the hydrogen bonds are not as strong as the hydroxyl bridge in compounds A or B. Upon lowering the sample temperature to $-40°$, the broad NH signal at δ = 14.2 ppm gradually assumes the appearance of a poor quartet. This signal can thereby be assigned to the proton residing on the methyl-substituted nitrogen. From the presence of a 5.0-Hz spin coupling of the N-methyl group, it is evident that the proton is on the nitrogen with little exchange to sulfur.

These results suggest that sulfur is as able as oxygen to participate in the unusual cross-conjugation and hydrogen bonding in these systems. This conclusion is in agreement with the studies of Marcus, *et al.*,[4] on simpler compounds.

(3) J. Goerdeler and U. Keuser, *Chem. Ber.*, **97**, 2209 (1964).
(4) S. H. Marcus, W. F. Reynolds, and S. I. Miller, *J. Org. Chem.*, **31**, 1872 (1966).
(5) S. H. Marcus and S. I. Miller, *J. Am. Chem. Soc.*, **88**, 3719 (1966).

Experimental Section

The two compounds, 4,4-dimethyl-2,6-dioxothiocyclohexanecarboxanilide (B, R = C_6H_5) and 4,4-dimethyl-2-(methylamino)-6-oxothio-1-cyclohexene-1-carboxanilide (C) were prepared as described by Goerdeler and Keuser[3] and have the physical properties reported by them.

The compound N-ethyl-4,4-dimethyl-2,6-dioxothiocyclohexanecarboxamide (B, R = C_2H_5) has not been reported. It was prepared similar to the others,[3] and crystallized from hexane. After sublimation, it melted at 54.6–55.4°. *Anal.* Calcd for $C_{11}H_{17}NO_2S$: C, 58.12; H, 7.54; N, 6.16; S, 14.11. Found: C, 58.48; H, 7.51; N, 6.17; S, 14.20.

In a similar manner N-methyl-4,4-dimethyl-2,6-dioxothiocyclohexanecarboxamide (B, R = CH_3) was prepared. It melted at 138.8–139.6°. *Anal.* Calcd for $C_{10}H_{15}NO_2S$: C, 56.31; H, 7.09; N, 6.57; S, 15.03. Found: C, 56.70; H, 7.07; N, 6.63; S, 15.20.

The determination of spectra has been previously described.[1]

Registry No.—B (R = C_6H_5), 7721-63-3; B (R = C_2H_5), 7721-64-4; B (R = CH_3), 7721-65-5; A (R = C_6H_5), 7721-66-6; A (R = CH_3), 944-53-6; C (R = C_6H_5), 7721-68-8.

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Preparation of Novel Cyclohexadienonecarboxamides

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Phosgene would not react with 2,6-di-*t*-butyl-4-methylphenol (I) under normal conditions to form the corresponding chloroformate (II) because the phenolic hydroxyl group is shielded too much by the adjacent bulky *t*-butyl groups. The chloroformate was desired for subsequent reaction with methylamine to prepare 2,6-di-*t*-butyl-4-methylphenyl methylcarbamate (VI) as illustrated by A. This carbamate, which is a selective herbicide for use on turf grass, is readily produced by reaction of I with methyl isocyanate in the presence of amine catalysts.[1] (See Scheme I.)

Under special conditions and using potassium hydroxide, phosgene reacted to form 3,5-di-*t*-butyl-1-methyl-2,5-cyclohexadien-4-onecarboxylic acid chloride (III). The latter condensed with methylamine and dimethylamine, respectively, to form the corresponding crystalline amides (IV and V) in high purity. Sodium hydroxide did not affect the formation of III even under the conditions successfully used with potassium hydroxide. Tertiary amines, which normally serve as acid acceptors for aryl chloroformate formation,[2] were also ineffective. Only when potassium hydroxide was employed initially to form an anhydrous salt was a significant acidic product

(1) A. H. Haubein, U. S. Patent 3,140,167 (July 7, 1964), assigned to Hercules Powder Co.
(2) M. Matzner, R. P. Kurkjy, and R. J. Cotter, *Chem. Rev.*, **64**, 649 (1964).