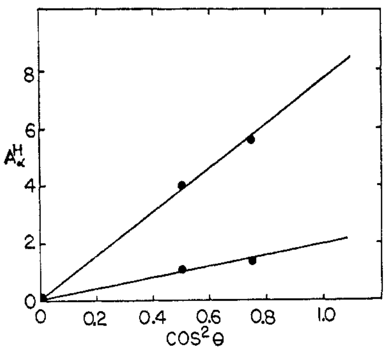

Figure 2.—Plots of *para* and *meta* α-hydrogen coupling constants *vs.* $\cos^2\theta$ for 2-nitrotriptycene (0 gauss, 90° and 0 gauss 90°), *p*-nitrotoluene (3.98 gauss, 45°), *m*-nitrotoluene (1.10 gauss, 45°), and 5-nitroindan (5.40 gauss, 30° and 1.38 gauss, 30°).

was attempted. Only very transient, free-radical species were obtained or no signal at all. However, the bright red or blue color characteristic of the carbanion was observed immediately after electrolysis was begun. It appears that the initially formed radicals act as strong bases and immediately remove the acidic proton from the parent *p*-nitrobenzyl derivative. Since the neutral reduced nitrobenzene radical formed by the protonation of nitrobenzene radical anion is not stable[14] no radicals are seen and simultaneously the unreduced *p*-nitrobenzyl derivative is removed from the solution and converted to the carbanion, *e.g.*

$$(C_6H_5)_2\text{—CH—}C_6H_4NO_2^{-}\cdot + (C_6H_5)_2\text{—CH—}(C_6H_4NO_2) \longrightarrow$$
$$\underset{\text{unstable}}{(C_6H_5)_2\text{—CH—}C_6H_4\dot{N}O_2H} + \underset{\text{stable carbanion}}{(C_6H_5)_2\text{—}\ddot{C}\text{—}C_6H_4NO_2^{-}}$$

Reduction of the carbanion is not possible by electrolysis. *p*-Nitrobenzyl bromide and *p*-nitrobenzyl phenyl ether also did not give stable radicals presumably because of elimination of bromide and phenoxide and ions.[15] The only useful spectrum was obtained from *p*-nitrophenylacetic acid. The coupling constants for this radical in acetonitrile are $a_N = 10.78$, $a_{2,6}{}^H = 3.23$, $a_{3,5}{}^H = 1.03$, $a^H = 2.84$. The radical is undoubtedly *p*-nitrophenylacetate dianion radical. Since the coupling constant of the α-methylene hydrogen is essentially the same as in *p*-ethylnitrobenzene, it would appear from this limited data that the carboxylate group is sterically and electronically similar to the methyl group in this solvent. This result is unexpected.

Electron spin resonance spectra were obtained with a Varian 4502 epr spectrometer with 12-in. magnet and "Fieldial" magnetic field control. Radicals were generated electrolytically in a Varian flat cell in acetonitrile containing tetraethylammonium perchlorate as carrier electrolyte. The electrode potential was increased slowly by small increments until radicals were detected. Since at similar potentials the well-known spectrum for nitrobenzene radical anion could be obtained no attempt was made to determine accurate reduction potentials for the nitrobenzene derivations discussed here. Representative values can be found in ref 11 and 13. The method for generating substituted nitrobenzene radical anions in dimethyl sulfoxide (80%)-*t*-butyl alcohol (20%) has been previously described.[16]

p-Nitrotoluene, *p*-nitroethylbenzene, and *p*-nitrocumene were obtained from commercial sources. A generous sample of 2-nitrotriptycene was obtained from Dr. R. L. Little.[17]

Registry No.—Acetonitrile, 75-0-58; 2-nitrotriptycene, 4628-55-1; *p*-nitrotoluene, 99-99-0; *m*-nitrotoluene, 99-08-1; 5-nitroindan, 7436-07-9; *p*-nitroethylbenzene, 100-12-9; *p*-isopropylnitrobenzene, 1817-47-6; methyl *p*-nitrophenylacetate, 2945-08-6; *p*-nitrophenylacetonitrile, 555-21-5; *p*-*p*′-dinitrodiphenylmethane, 1817-74-9; *p*-nitrophenyldiphenylmethane, 2945-12-2; tris(*p*-nitrophenyl)methane, 603-49-6; *p*-nitrobenzyl bromide, 100-11-8; *p*-nitrobenzyl phenyl ether, 3048-12-2; *p*-nitrophenylacetic acid, 104-03-0; tetraethylammonium perchlorate, 2567-83-1; 3,4-dimethylnitrobenzene, 99-51-4.

Acknowledgment.—Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[14] R. L. Ward, *J. Chem. Phys.*, **38**, 2588 (1963).

[15] R. C. Kerber, G. W. Urry, and N. Kornblum, *J. Am. Chem. Soc.*, **87**, 4520 (1965).

[16] G. A. Russell, E. G. Janzen, and E. T. Strom, *ibid.*, **86**, 1807 (1964); G. A. Russell, E. G. Janzen, A. G. Bemis, E. J. Geels, A. J. Moye, A. Mak, and E. T. Strom in "Selective Oxidation Processes," Advances in Chemistry Series, 51, American Chemical Society, Washington, D. C., 1965, p 112.

[17] We acknowledge Dr. Little's original suggestion which prompted the investigation of the esr spectrum of 2-nitrotriptycene anion radical.

Infrared Spectra of N^{15}-Substituted Schiff Bases

GERALD DUDEK

Department of Chemistry, Harvard University, Cambridge, Massachusetts

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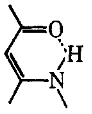
The interpretation of the infrared spectra of chelated α,β-unsaturated β-ketamines has been difficult owing to strong interactions between the carbonyl, the carbon–carbon double bond, and the amino vibrations which may render the concept of group frequencies unapplicable in these systems.[1–4]



Kinseley, *et al.*,[3] demonstrated that N^{15} labeling provided valuable information for the interpretation of the spectra of amides as the band shift between the N^{14} and N^{15} compounds established the C–N frequencies.[3,5] Accordingly, the infrared spectra of several N^{15}-labeled Schiff bases[6] have been obtained

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[1] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1958.

[2] J. Dabrowski. *Spectrochim. Acta*, **19**, 475 (1963).

[3] R. N. Kniseley, V. A. Fassel, E. L. Farquhar, and L. S. Gray, *ibid.*, **18**, 1217 (1962).

[4] H. Holtzclaw, J. P. Collman, and R. M. Alire, *J. Am. Chem. Soc.*, **80**, 1100 (1958).

[5] M. Tsuboi, *Spectrochim. Acta*, **16**, 505 (1960).

[6] G. Dudek and E. P. Dudek, *J. Am. Chem. Soc.*, **86**, 4283 (1964); *ibid.*, **88**, 2407 (1966).

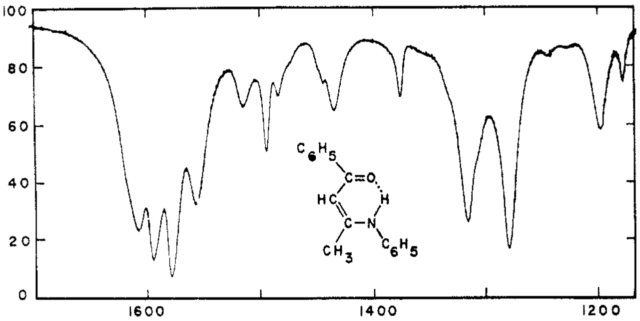


Figure 1.—The infrared spectrum of 3-(N-methylamino)crotonophenone (CCl_4 solution).

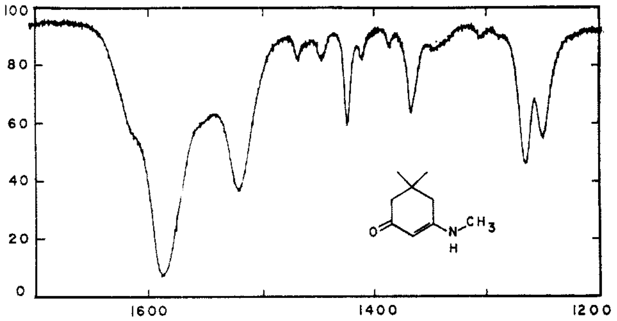


Figure 2.—The infrared spectrum of 3-(N-methylamino)-5,5-dimethylcyclohexen-1-one ($CDCl_3$ solution).

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.)

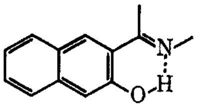
Table I

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-dimethylcyclohen-1-one, 701-58-6; III, 7721-60-0.

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

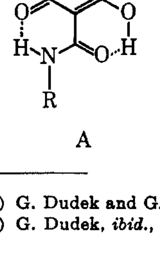
The Proton Magnetic Resonance Spectra of Thiocarboxamides

Emily Pitcher Dudek and Gerald Dudek

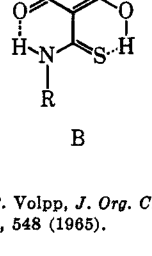
Departments of Chemistry, Wellesley College, Wellesley, Massachusetts, and Harvard University, Cambridge, Massachusetts

Received September 20, 1966

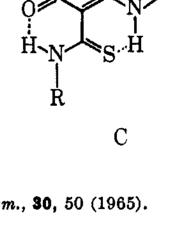
The β-diketamide group common to N-substituted 2-carbamoyldimedone derivatives (A) is an unusual cross-conjugated system.[1] Proton magnetic resonance (pmr) spectra indicate that the compounds are enolic and that the enolic and the amino hydrogens are involved in *strong* hydrogen bonding as evidenced 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

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[1] G. Dudek and G. P. Volpp, *J. Org. Chem.*, **30**, 50 (1965).

[2] G. Dudek, *ibid.*, **30**, 548 (1965).