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The Donor Properties of Some Carbonyl Compounds¹BY RICHARD L. MIDDAUGH,^{1b} RUSSELL S. DRAGO, AND ROBERT J. NIEDZIELSKI^{1c}

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Heats of formation for adducts of *N,N*-dimethyltrifluoroacetamide, tetramethylurea, methyl acetate, and *S*-methyl thioacetate with phenol are reported. Thermodynamic data were obtained for adducts of tetramethylurea, methyl acetate, *S*-methyl thioacetate, and acetone with iodine. The effect of π -bonding on these donor properties is discussed. Tetramethylurea was investigated to determine whether or not the π -system is delocalized over both of the nitrogens and the carbonyl group in this molecule. The measured donor properties of this compound and *N,N*-dimethylacetamide are compared with those predicted from approximate m.o. calculations of the Hückel type. The donor properties of methyl acetate and *S*-methyl thioacetate provide a comparison of the effects of the substituents NR_2 , OR, and SR on the carbonyl oxygen donor properties. The results indicate that the coordinating properties of tetramethylurea as a nonaqueous solvent are about the same as those of *N,N*-dimethylacetamide, whereas those of acetates and thioacetates are much weaker. The n.m.r. spectra of some substituted amides, $\text{XC(O)N(CH}_3)_2$, where X is a group capable of π -bonding to the carbonyl group, are given, and the barriers to C–N rotation in these compounds are discussed.

Introduction

In earlier articles, studies of the donor properties of some carbonyl compounds have been reported.^{2–12} Systems that are soluble in CCl_4 have been chosen in order to eliminate any significant contributions to thermodynamic data from solvation effects. Donor properties of acetone and dimethylacetamide toward iodine and phenol indicate that the substitution of an NR_2 group onto a carbonyl group produces an increase in the donor ability of the carbonyl oxygen nonbonding electrons. This is attributed to delocalization of the nonbonding electron pair on the nitrogen into a π -molecular orbital involving all three atoms (O, C, and N) of the amide functional group.² For amides of the general formula $\text{RC(O)NR}'_2$, the carbonyl donor strengths are sensitive to inductive and conjugative (π -bonding) effects of both R and R' substituents. Heats of formation for phenol and iodine adducts with a series of *N,N*-dimethylamides, $\text{RC(O)N(CH}_3)_2$, have been correlated with Taft's σ^* values for non-conjugating R substituents.^{6,9} Heats of formation for iodine adducts with a series of *para*-substituted *N,N*-dimethylbenzamides¹⁰ and with a series of *ortho*-substituted *N*-methylacetanilides¹² have been correlated with Hammett's σ constants for the substituents. Amide-type donors reported in this study are *N,N*-dimethyltrifluoroacetamide, $\text{CF}_3\text{C(O)N(CH}_3)_2$, and tetramethylurea, $(\text{CH}_3)_2\text{NC(O)N(CH}_3)_2$. In the latter compound, there is the possibility of the extension of the delocalized π -system to include the second NR_2 group and its unshared electron pair.

The present investigation includes a study of the effect on carbonyl donor properties of substituents other than NR_2 but which also have unshared electron pairs that might be capable of a similar π -interaction with the carbonyl group.

Experimental

Reagents.—Solvents, used without further purification, were Fisher Spectranalyzed CCl_4 , Eastman Spectro grade CH_2Cl_2 , and Mallinckrodt analytical reagent toluene.

(1) (a) Abstracted in part from the Ph.D. Thesis (Univ. of Ill.) of R. J. Niedzielski (1962) and R. L. Middaugh (1964); (b) National Science Foundation Graduate Fellow, 1962–1964; (c) August Kochs Fellow, 1961–1962.

(2) C. D. Schmulbach and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 4484 (1960).

(3) R. S. Drago, R. L. Carlson, N. J. Rose, and D. A. Wenz, *ibid.*, **83**, 3572 (1961).

(4) R. S. Drago and D. Bafus, *J. Phys. Chem.*, **65**, 1066 (1961).

(5) R. S. Drago and D. A. Wenz, *J. Am. Chem. Soc.*, **84**, 526 (1962).

(6) R. S. Drago, D. A. Wenz, and R. L. Carlson, *ibid.*, **84**, 1106 (1962).

(7) M. D. Joesten and R. S. Drago, *ibid.*, **84**, 2037 (1962).

(8) R. L. Carlson and R. S. Drago, *ibid.*, **84**, 2320 (1962).

(9) M. D. Joesten and R. S. Drago, *ibid.*, **84**, 2696 (1962).

(10) R. L. Carlson and R. S. Drago, *ibid.*, **85**, 505 (1963).

(11) R. S. Drago, D. W. Meek, M. D. Joesten, and L. LaRoche, *Inorg. Chem.*, **2**, 124 (1963).

(12) R. S. Drago and R. L. Carlson, to be published.

Phenol was distilled at atmospheric pressure, the material boiling at 182° being collected. This was then sublimed just before use.

The procedure for the purification of iodine has been described elsewhere.²

N,N-Dimethyltrifluoroacetamide was prepared by saturating methyl trifluoroacetate with dimethylamine at –7° and allowing it to stand at room temperature for 12 hr.¹³ Distillation gave an 81% yield of $\text{CF}_3\text{C(O)N(CH}_3)_2$ boiling at 134.5–136.0°.

Tetramethylurea (K and K Laboratories, Inc.) was used without further purification.

Anal. Calcd. for $\text{C}_4\text{H}_{12}\text{N}_2\text{O}$: C, 51.70; H, 10.41; N, 24.12. Found: C, 51.83; H, 10.52; N, 23.87.

Methyl acetate (Eastman) was distilled and the fraction boiling at 57.0–57.1° (uncor.) was collected and stored over Linde Type 3A Molecular Sieves. No impurity was detectable by vapor phase chromatography.

S-Methyl thioacetate was prepared from acetyl chloride and methanethiol.¹⁴ After repeated distillations, a fraction boiling at 96.5–97.0° was used.

Anal. Calcd. for $\text{C}_3\text{H}_6\text{OS}$: C, 39.97; H, 6.71. Found: C, 40.06; H, 6.86.

Analytical reagent acetone (Mallinckrodt) was used without further purification.

The compound $\text{CH}_3\text{SC(O)Cl}$ was prepared from phosgene and methane thiol. This product was allowed to react with dimethylamine¹⁶ to give $\text{CH}_3\text{SC(O)N(CH}_3)_2$, b.p. 55° (5 mm.).

Anal. Calcd. for $\text{C}_4\text{H}_9\text{NOS}$: C, 40.30; H, 7.61; N, 11.26. Found: C, 40.40; H, 7.71; N, 11.75.

Methyl chloroformate and dimethylamine¹⁶ gave $\text{CH}_3\text{OC(O)N(CH}_3)_2$, b.p. 56.5–57.0° (38 mm.).

Anal. Calcd. for $\text{C}_4\text{H}_9\text{O}_2\text{N}$: C, 46.60; H, 8.80; N, 13.59. Found: C, 47.20; H, 8.74; N, 12.55.

Apparatus and Procedure.—Descriptions of apparatus and procedures for determination of phenol frequency shifts¹⁷ and thermodynamic data of iodine adducts³ have been published. The acetone-iodine equilibrium constant was determined on a Bausch and Lomb Spectronic 505 spectrophotometer, using 5-cm. cells.

Carbonyl frequency shifts were obtained using a Perkin-Elmer Model 21 infrared spectrometer.

The n.m.r. spectra were obtained with a Varian Model A-60 n.m.r. spectrometer, with the exception of the low temperature spectra, which were obtained with a Varian Model DP-60 n.m.r. spectrometer.

TABLE I
ADDUCTS WITH PHENOL IN CCl_4

Base	$\Delta\nu_{\text{OH}}$, cm.^{-1} ^a	$-\Delta H$, kcal./mole
$\text{CF}_3\text{C(O)N(CH}_3)_2$	185	3.6 ± 0.4
$(\text{CH}_3)_2\text{NC(O)N(CH}_3)_2$	338	$6.0 \pm .4$
$\text{CH}_3\text{C(O)OCH}_3$	170	$3.3 \pm .4$
$\text{CH}_3\text{C(O)SCH}_3$	162	$3.2 \pm .4$
$\text{CH}_3\text{C(O)N(CH}_3)_2$	342	$6.1 \pm .4$
$\text{C}_6\text{H}_5\text{C(O)N(CH}_3)_2$	283	$5.2 \pm .4$
$\text{CH}_3\text{C(O)CH}_3$	193	$3.7 \pm .4$

^a For free phenol, ν_{OH} 3609 cm.^{-1} . All phenol concentrations were approximately 0.15 *M*. Base concentrations were sufficient to complex about 75% of the phenol (1 *M* or less).

(13) E. R. Bissell and M. Finger, *J. Org. Chem.*, **24**, 1256 (1959).

(14) F. Arndt, I. Loewe, and M. Ozansoy, *Ber.*, **72B**, 1862 (1939).

(15) R. Riemschneider and O. Lorenz, *Monatsh. Chem.*, **84**, 518 (1953).

(16) W. W. Hartman and M. R. Brethen, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, New York, N. Y., 1943, p. 278.

Results

Donor Strengths. (A) Toward Phenol.—It has been shown that for hydrogen-bonded 1:1 adducts of phenol with a large number of widely different bases, the shift in the O-H stretching frequency can be used to measure the enthalpy of formation of the adduct.^{17,18} This relationship is particularly well established for

TABLE II
SPECTROPHOTOMETRIC DATA FOR IODINE ADDUCTS IN CCl₄

Donor	λ , m μ	T , °C.	C_I , mole/l. ^a	C_D , mole/l. ^b	$A - A_0^c$
(CH ₃) ₂ NC(O)N(CH ₃) ₂	550	25.0	0.00172	0.0192	-0.109
				.0384	-.197
				.0769	-.326
(CH ₃) ₂ NC(O)N(CH ₃) ₂	550	25.0	.00160	.0177	-.095
				.0355	-.173
				.0710	-.292
(CH ₃) ₂ NC(O)N(CH ₃) ₂	472	25.0	.00172	.0192	.126
				.0384	.226
				.0769	.381
(CH ₃) ₂ NC(O)N(CH ₃) ₂	472	25.0	.00160	.0177	.113
				.0355	.205
				.0710	.347
CH ₃ C(O)OCH ₃	550	25.0	.001912	.1244	-.055
				.2487	-.104
				.4974	-.186
CH ₃ C(O)SCH ₃	550	25.0	.00372	.0881	-.091
				.1762	-.171
				.3524	-.307
CH ₃ C(O)SCH ₃	550	25.0	.00357	.0843	-.082
				.1686	-.158
				.3373	-.286
CH ₃ C(O)SCH ₃	550	25.0	.00303	.0624	-.052
				.1247	-.099
				.2494	-.189
CH ₃ C(O)SCH ₃	550	25.0	.00304	.0554	-.047
				.1108	-.091
				.2217	-.169
(CH ₃) ₂ NC(O)N(CH ₃) ₂	550	24.8	.00172	.0384	-.199
				.0769	-.383
				.1154	-.574
				.1539	-.765
				.1924	-.956
				.2309	-1.147
				.2694	-1.338
				.3079	-1.529
				.3464	-1.720
				.3849	-1.911
				.4234	-2.102
				.4619	-2.293
				.5004	-2.484
CH ₃ C(O)OCH ₃	550	30.5	.001900	.4942	-.172
				.4916	-.163
				.4886	-.152
				.4857	-.143
				.4827	-.134
CH ₃ C(O)SCH ₃	550	24.4	.00372	.3526	-.315
				.3513	-.300
				.3500	-.285
				.3487	-.271
				.3474	-.259
				.3462	-.247
				.3450	-.235
				.3437	-.221
				.3424	-.209
				.3412	-.197
				.3400	-.185
				.3387	-.173
				.3375	-.161
CH ₃ C(O)SCH ₃	550	25	.000109	.113	-.030 ^d
				.226	-.055 ^d
				.340	-.080 ^d
				.453	-.105 ^d
				.566	-.130 ^d
				.679	-.155 ^d
				.792	-.180 ^d
				.905	-.205 ^d
				1.018	-.230 ^d
				1.131	-.255 ^d
				1.244	-.280 ^d
				1.357	-.305 ^d
				1.470	-.330 ^d

^a Total concentration of iodine. ^b Total concentration of base. ^c Absorbance of 1 cm. of adduct solution measured against a blank consisting of C_I molar iodine in CCl₄. ^d Path length 5 cm.

(17) M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962).
(18) H. Drinken and H. Fritzsche, *Z. Chem.*, **2**, 345 (1962); F. Gramstad, *Spectrochim. Acta*, **19**, 829 (1963), and previous papers in this series.

oxygen donors with phenol, the subject of this paper. Frequency shifts and the corresponding ΔH values for some phenol adducts are given in Table I.

(B) Toward Iodine.—Spectrophotometric data for the iodine adducts are given in Table II. The treatment of such data to give equilibrium constants and enthalpies of formation has been described.^{3,19} The results of these calculations are given in Table III.

TABLE III
THERMODYNAMIC DATA FOR IODINE ADDUCTS IN CCl₄

Donor	λ , m μ	$\epsilon C - \epsilon I$	K_{25} , l./mole	$-\Delta H$, kcal./ mole ^a
(CH ₃) ₂ NC(O)N(CH ₃) ₂	550	-585	6.5 ± 0.2	4.3 ± 0.1
	472	677	6.5 ± 0.2	4.4 ± 0.2
CH ₃ C(O)OCH ₃	550	-478	0.52 ± 0.03	2.5 ± 0.1
CH ₃ C(O)SCH ₃	550	-410	0.72 ± 0.10	3.15 ± 0.12
CH ₃ C(O)N(CH ₃) ₂ ^b			6.9 ± 0.2	4.0 ± 0.1
CH ₃ C(O)CH ₃	550	-612	0.85 ± 0.1	

^a Uncertainties in ΔH calculated at the 95% confidence level. ^b See ref. 3.

A lowering of the frequency of the predominantly C-O stretching mode of carbonyl compounds upon adduct formation is evidence that the donor site is the carbonyl oxygen.² The infrared spectral data summarized in Table IV indicate that in each case, the carbonyl oxygen is the donor site. There was no evidence of increased absorption on the high frequency side of the free carbonyl absorption which would be expected for nitrogen coordination.

TABLE IV
CARBONYL FREQUENCY SHIFTS FOR IODINE ADDUCTS IN CCl₄

Donor	ν_{CO} (free), cm. ⁻¹	ν_{CO} (complex), cm. ⁻¹	$\Delta\nu_{CO}$, cm. ⁻¹
(CH ₃) ₂ NC(O)N(CH ₃) ₂	1653	1605	48
CH ₃ C(O)N(CH ₃) ₂ ^a	1658	1615	43
C ₆ H ₅ C(O)N(CH ₃) ₂ ^b	1640	1600	40
CH ₃ C(O)SCH ₃	1696	1688	8
CH ₃ C(O)CH ₃ ^a	1717	1701	16

^a See ref. 2. ^b R. L. Carlson, Thesis, University of Illinois, 1962.

Molecular Orbital Calculations.—Approximate m.o. calculations of the Hückel type, neglecting overlap, were made for the π -systems of the amide and urea skeletons. The parameters used in the calculations and the results obtained are listed in Table V. The

TABLE V
MOLECULAR ORBITAL CALCULATIONS FOR π -SYSTEMS^a

Amide ^b	Urea
$\alpha_C = \alpha$	$\alpha_C = \alpha$
$\alpha_N = \alpha + 0.7\beta$	$\alpha_N = \alpha + 0.7\beta$
$\alpha_O = \alpha + 1.1\beta$	$\alpha_O = \alpha + 1.1\beta$
$\beta_{CN} = 0.8\beta$	$\beta_{CN} = 0.8\beta$
$\beta_{CO} = 0.9\beta$	$\beta_{CO} = 0.9\beta$
$Q_C = +0.35$	$Q_C = +0.26$
$Q_N = +.32$	$Q_N = +.22$
$Q_O = -.67$	$Q_O = -.75$
$p_{CO} = 0.48$	$p_{CO} = 0.31$
$p_{CN} = 0.52$	$p_{CN} = 0.34$

^a α_i = coulomb integral of atom i ; β_{ij} = exchange integral between atoms i and j ; Q_i = effective charge on atom i , due to π -electron distribution; p_{ij} = π -bond order between atoms i and j normalized so that $\sum p = 1$, considering only directly-bonded terms. ^b See ref. 20 for the effect of small changes in α and β values on results in the amide system.

(19) N. J. Rose and R. S. Drago, *J. Am. Chem. Soc.*, **81**, 6138 (1959).

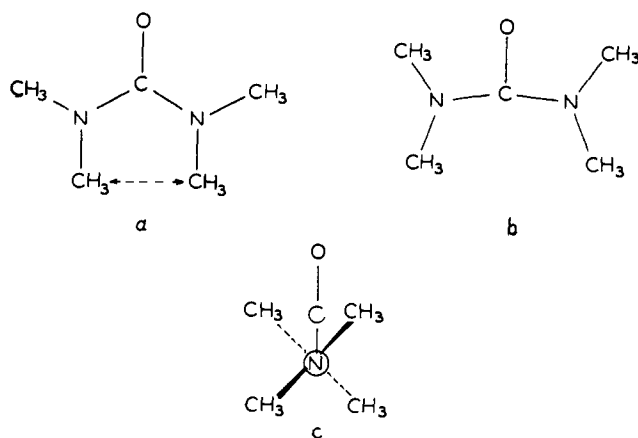


Fig. 1.—(a) TMU with bond angles 120° , showing steric strain between methyl groups in planar configuration. (b) Steric strain relieved by distortion of bond angles in planar configuration. (c) Steric strain relieved by rotation of NR_2 groups to give a nonzero dihedral angle between NR_2 planes.

results for the amide system agree with those of Nagakura.²⁰

N.m.r. Spectra.—Chemical shifts for the methyl groups of some carbonyl compounds dissolved in CCl_4 are given in Table VI. In the same table are listed the barriers to rotation about the C–N bond of some *N,N*-dimethylamides as determined by Rogers and Woodbrey from the temperature dependence of the separation between the two different N-methyl n.m.r. signals of the pure liquids.^{21a}

TABLE VI
NUCLEAR MAGNETIC RESONANCE SPECTRA

	τ , p.p.m. ^a	E_a , kcal./mole ^b
$(\text{CH}_3)_2\text{NC}(\text{O})\text{N}(\text{CH}_3)_2$	7.27	
$\bullet\text{CH}_3\text{SC}(\text{O})\text{N}(\text{CH}_3)_2^b$	a, 7.72	
	b, 7.00	
$\bullet\text{CH}_3\text{OC}(\text{O})\text{N}(\text{CH}_3)_2^b$	a, 6.40	
	b, 7.13	
$\text{CF}_3\text{C}(\text{O})\text{N}(\text{CH}_3)_2$	6.84, 6.96	9.3
$\bullet\text{CH}_3\text{C}(\text{O})\text{N}(\text{CH}_3)_2^b$	a, 8.03	10.6
	b, 6.98, 7.17	
$\text{C}_6\text{H}_5\text{C}(\text{O})\text{N}(\text{CH}_3)_2$		7.7
$\text{CH}_2=\text{CHC}(\text{O})\text{N}(\text{CH}_3)_2$		6.8
$\text{ClC}(\text{O})\text{N}(\text{CH}_3)_2$		7.3
$\text{C}_2\text{H}_5\text{OC}(\text{O})\text{N}(\text{CH}_3)_2$	One signal only	

^a Chemical shift in CCl_4 relative to internal tetramethylsilane at 10,000 p.p.m. ^b Determined by Rogers and Woodbrey, ref. 21a. These values cannot be compared with each other directly because they were determined in different solvents, *i.e.*, the pure liquids. The same authors have indicated the significance of the solvent effect.^{21b}

The n.m.r. spectra of $(\text{CH}_3)_2\text{NC}(\text{O})\text{N}(\text{CH}_3)_2$, $\text{CH}_3\text{OC}(\text{O})\text{N}(\text{CH}_3)_2$, and $\text{CH}_3\text{SC}(\text{O})\text{N}(\text{CH}_3)_2$ were examined at room temperature for the pure liquids and for 10% solutions in benzene, CCl_4 , and CCl_4 -benzene (50% by volume) and at -46° for 25% solutions in methylene chloride and toluene. In all cases, a single sharp resonance signal for the N-methyl protons was observed.

Discussion

Donor Properties of *N,N*-Dimethylamides and Tetramethylurea.—The heats of formation of adducts with iodine and with phenol have been correlated with Taft's polar substituent constants, σ^* , for a series of amides $\text{RC}(\text{O})\text{N}(\text{CH}_3)_2$, where R is a nonconjugating

substituent.^{6,9} In *N,N*-dimethyltrifluoroacetamide the strong electron-withdrawing property of the CF_3 group is evident. The increase in the donor ability of the carbonyl oxygen attributable to the π -interaction of the NR_2 group is offset by the inductive effect of the CF_3 group, so that *N,N*-dimethyltrifluoroacetamide is equivalent to acetone as a donor toward phenol (Table I).

Urea has been shown to have a completely planar structure.²² Assuming a planar $\text{C}_2\text{NC}(\text{O})\text{NC}_2$ skeleton for tetramethylurea and a planar $\text{CC}(\text{O})\text{NC}_2$ skeleton for dimethylacetamide, m.o. calculations were carried out which indicate there is considerably greater π -electron density on the oxygen in tetramethylurea than in dimethylacetamide. This difference (0.08 unit of charge) is of the same order of magnitude as the difference (0.12 unit) between the calculated charge on the oxygen in a ketone (-0.55)²⁰ and an amide. In both cases there is the opposing inductive effect of the NR_2 group partially offsetting the effect of the π -interaction. Comparison of the donor abilities of acetone and dimethylacetamide shows that a π -interaction of this magnitude is much stronger than the inductive effect of the NR_2 group. On this basis, tetramethylurea would be expected to be a much better donor than dimethylacetamide, a prediction not borne out by the observed heats with iodine and phenol (Tables I and III).

A Fisher-Taylor-Hirschfelder model of tetramethylurea using trigonal nitrogen and carbonyl carbon atoms indicates a significant amount of steric interference between methyl groups on different nitrogens in the planar configuration (see Fig. 1a). Such steric strain could be relieved by distortion of the bond angles at the nitrogens or at the carbonyl carbon (Fig. 1b) or by rotating one or both of the NR_2 groups out of the carbonyl plane (Fig. 1c). Increasing the N–C–N angle would weaken the C=O bond by employing more of the carbon s-orbital in the bonds to nitrogen and less in the bond to oxygen. This effect would increase the donor ability of the oxygen nonbonding electrons,²³ in conflict with the observed heats of formation. If the NR_2 groups are not coplanar, however, part of the π -overlap between the nitrogens and the carbonyl group is lost and the donor ability of the oxygen would then be less than that predicted for planar tetramethylurea.

Janssen has examined the ultraviolet spectra of the series of methyl-substituted thioureas.²⁴ The spectra of thiourea and mono-, di-, and trimethylthiourea are all similar, but that of tetramethylthiourea differs from these. By placing the methyl substituents preferentially *cis* to the thiocarbonyl sulfur in a planar structure, the steric repulsion of methyl groups would be avoided in all but the completely substituted molecule. The molecular structures of tetramethylthiourea and tetramethylurea are similar, so that this evidence of a steric effect in tetramethylthiourea is applicable also to tetramethylurea. The bulk of the evidence supports the structure for tetramethylurea indicated in Fig. 1c.

Donor Properties of Other Carbonyl Compounds.—The substitution of an OR group onto a carbonyl group does not increase the donor ability of the carbonyl oxygen (see Table I), although there are unshared electron pairs on the OR group capable of amide-like π -delocalization into the carbonyl system. The magnitude and temperature-independence of the dipole moment of methyl acetate show the existence of a

(22) P. Vaughan and J. Donoghue, *Acta Cryst.*, **5**, 530 (1952); E. R. Andrew and D. Hyndman, *Discussions Faraday Soc.*, **19**, 195 (1955); J. E. Worsham, Jr., H. A. Levy, and S. W. Peterson, *Acta Cryst.*, **10**, 319 (1957).

(23) D. Cook, *Can. J. Chem.*, **39**, 31 (1961).

(24) M. J. Janssen, *Rec. trav. chim.*, **79**, 454 (1960).

(20) S. Nagakura, *Bull. Chem. Soc. Japan*, **25**, 164 (1952).

(21) (a) M. T. Rogers and J. C. Woodbrey, *J. Phys. Chem.*, **66**, 540 (1962);

(b) J. C. Woodbrey and M. T. Rogers, *J. Am. Chem. Soc.*, **84**, 13 (1962).

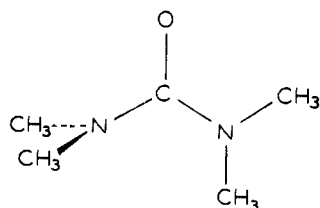


Fig. 2.—Transition state for C-N rotation in tetramethylurea. Atoms NC(O)NC₂ are coplanar.

substantial barrier to rotation about the bond between the carbonyl and OR groups, indicating appreciable π -bonding.²⁵ This has been confirmed by electron diffraction²⁶ and is supported by a study of the microwave spectrum of methyl formate which indicated an approximately coplanar carbon, oxygen skeleton.²⁷ From the low-frequency infrared spectrum, Miyazawa has calculated a barrier to rotation of about 16 kcal./mole for methyl acetate, approximately the same as for N-methylacetamide.²⁸ From these studies and from the donor properties of methyl acetate we conclude that there is significant π -bonding in the ester, but that its effect is offset by the rather strongly electron-withdrawing inductive effect of the OR group compared to that of the NR₂ groups (see Taft's inductive substituent constants, Table VII).

TABLE VII
TAFT'S σ^* AND σ_I CONSTANTS

	σ^{*a}	σ_I^b
CH ₃ -	0.00	-0.05
H-	+ .49	.00
C ₆ H ₅ -	+ .60	+ .10
(CH ₃) ₂ N-		+ .10
CH ₃ O-		+ .25
CH ₃ S-		+ .25
CF ₃ -		+ .41

^a R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 556-675. ^b R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **80**, 2436 (1958).

The donor ability of S-methyl thioacetate toward phenol is about the same as that of methyl acetate (Table I), but S-methyl thioacetate is a slightly stronger donor toward iodine than is methyl acetate (Table III). This is consistent with the SR group having about the same inductive effect as the OR group (see Table VII), balanced by about the same amount of π bonding. Because the interaction of a donor with iodine derives a greater proportion of its strength from covalence or charge-transfer than does the interaction with phenol, it is more sensitive to the ease of polarization or distortability of the electronic structure of the donor. For example, oxygen donors are stronger toward phenol than structurally analogous sulfur donors, but the reverse is true toward iodine as the acid.²⁹ The relatively small difference between the donor abilities of S-methyl thioacetate and methyl acetate toward iodine is reasonable, because the sulfur in S-methyl thioacetate is not the donor atom. The carbonyl oxygen will be affected by the polarization of the sulfur through either or both the σ and π systems.

The spectra of CCl₄ solutions containing acetone and iodine changed with time, indicating that a reaction was taking place. For this reason, only an approxi-

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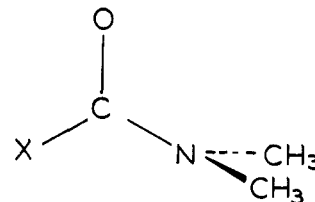


Fig. 3.—Transition state for internal rotation. Plane NCC is perpendicular to plane XCON.

mate equilibrium constant at room temperature was obtained for this system. The result agrees with that determined from infrared measurements.²

An important property of amides as nonaqueous solvents is their coordinating power or donor ability. The results presented above indicate that tetramethylurea will have similar coordinating properties to those of N,N-dimethylacetamide, whereas esters and thioesters will have weaker coordinating tendencies.

N.m.r. Spectra of N,N-Dimethylamides.—Rogers and Woodbrey observed that the compound C₂H₅OC(O)N(CH₃)₂ had only one N-methyl signal at temperatures down to its freezing point.^{21a} Two possible explanations were offered, both invoking "cross-conjugation," or π -interaction of the C₂H₅O group with the amide system. This π -interaction could weaken the C-N π -bonding enough to make the barrier to rotation too small to be observed by this method. It would also make the two C-O bonds more nearly alike in their anisotropy, resulting in a chemical shift between the two N-methyl groups that might be too small to have been detected. We have observed single N-methyl n.m.r. signals for tetramethylurea, N,N,S-trimethyl monothiocarbamate, and N,N,O-trimethyl carbamate, at room temperature in CCl₄, benzene, CCl₄-benzene (50% by volume), and as pure liquids, and for tetramethylurea at -46° in methylene chloride and toluene. It is well known that the relative chemical shifts of the two N-methyl groups in N,N-dimethylamides are solvent dependent, due to specific interactions of solvent molecules with the amide molecules.^{21b,30} We conclude that a low barrier to rotation about the C-N bond properly accounts for the single N-methyl signal in XC(O)N(CH₃)₂, where X = N(CH₃)₂, OCH₃, or SCH₃, because in none of the widely different solvent media used in this study was more than one N-methyl resonance signal observed. Identical chemical shifts for the two different planar N-methyl groups would require that the shielding due to magnetic anisotropy of the C-X bond and in the X-group itself fortuitously equal that of the C=O bond, where X is attached through a first-row element N or O and through the second-row element S. We consider it to be highly unlikely that for the carbamate, thiocarbamate, and urea structures, the chemical shifts of the two N-methyl groups in the planar configuration are coincident and equally affected by the different solvent-solute interactions.

The observation of a low barrier to rotation about the C-N bonds of tetramethylurea supports the model developed in the first section of the Discussion, that steric repulsion between methyl groups prevents tetramethylurea from having a completely planar C₂NCONC₂ skeleton, but that there is appreciable π -interaction of both NR₂ groups with the carbonyl system. If we assume a transition state in which one NR₂ group lies in a plane with the C-O bond and the other NR₂ group is perpendicular to that plane (see Fig. 2), its electronic structure will be similar to that of an amide, RCONR₂. There will be more resonance energy associated with the C-N π -bond in the transition state

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than with either C-N bond in the ground state configuration of tetramethylurea. The loss of the π bond energy of one C-N bond is at least partially recovered by the increased π -bonding to the other NR₂ group in the transition state; and a lower barrier to rotation is observed in tetramethylurea than in a simple amide, RCONR₂, in which all of the C-N π -bond energy is lost in the transition state.

It can be seen from the m.o. calculations summarized in Table V that the presence of a group, X, capable of π -bonding in XC(O)NR₂ reduces the amount of π -bonding in the C-N bond. Similarly, the presence of the NR₂ group will reduce the amount of C-X π -bonding compared to a compound of the type XC(O)R. The transition state for the C-N rotation which makes the N-methyl groups equivalent in the n.m.r. spectrum has the structure of a molecule XC(O)R, where R is a *nonconjugated* NR₂ group, illustrated in Fig. 3. For the cases X = NR₂, OR, and SR, the transition state will correspond to a substituted amide, ester, and thioester, respectively. We have seen earlier in the Discussion that there is a considerable amount of X-C π -bonding in molecules of these types. For X = OR

or SR in XC(O)NR₂, the loss of the C-N π -bonding energy in the transition state is partly compensated for by an increase in the X-C π -bonding. For X = alkyl, there is no π -bonding in the transition state to compensate for the loss of C-N π -bonding energy, so that the barrier to rotation is higher and is observed as two nonequivalent N-methyl n.m.r. signals. The above results conclusively indicate the occurrence of π -bonding between SR and the carbonyl group.

This resonance stabilization of the transition state will be accentuated in the case of tetramethylurea, by the steric effect discussed above. There is less π -bonding in the ground state configuration, due to the steric effect. In the transition state, this effect is not present, and there will be complete amide-type π -bonding to the nonrotating NR₂ group, giving greater resonance stabilization to the transition state than in molecules where the steric effect is less.

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