N-Nitroamides and N-Nitrocarbamates. III. Rotational Isomerism, Steric Effects, and Physical Properties at Low Temperatures[1]

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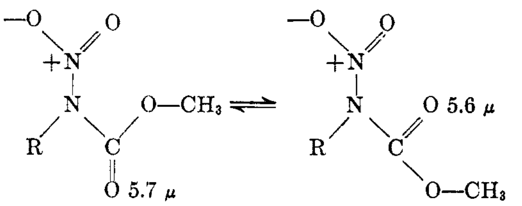
Infrared, ultraviolet, and nuclear magnetic resonance spectra (at room temperature and at low temperatures), solvent effects, and substituent effects have been used to show that the double carbonyl peaks of the N-nitrocarbamates stem from rotational isomerism involving the carboxyl groups, and not from Fermi resonance. Cyclic nitrocarbamates in which this type of rotation is impossible have only a single carbonyl band in the infrared. The rotation is frozen out at about −90°, and in the crystalline state only one conformer appears to be present; the two forms differ in energy by less than 1 kcal/mole. Seriously hindered nitrocarbamates show two carbonyl bands and two nitro bands in the stretching region of the infrared; the doubling of the band assigned to the asymmetric stretching mode of the nitro group is attributed to strong interactions between the nitro group and the two different oxygen atoms of the carbomethoxy group; serious departures of the molecule from coplanarity may also be involved. Similar evidence is used to show that the N-nitroamides exist largely in one conformation, the "transoid."

We have reported previously[2] on the preparation and decomposition of various N-nitrocarbamates. The infrared spectra of these compounds show two absorption bands in the carbonyl stretching region. We showed that the compounds were pure, not associated in solution, and that the splitting probably did not stem from Fermi resonance.[3] We then proposed that the N-nitrocarbamates exist as mixtures of two rotational isomers (eq 1), and that the forms have different carbonyl bands in the infrared. In the present paper we examine the problem in greater depth and present evidence that confirms and extends the earlier proposals.



I II (1)

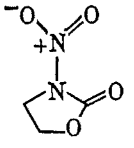
a, R = H
b, R = CH_3
c, R = $CH_3CH_2CH_2CH_2$
d, R = $CH_3CH_2CH(CH_3)$
e, R = $(CH_3)_3C$
f, R = $(CH_3CH_2)_3C$

N-Nitrocarbamates

A series of N-nitrocarbamates (I, IIa–f) was prepared by the nitration of the corresponding carbamates with nitric acid or with mixtures of nitric acid and acetic anhydride. Without exception, two carbonyl peaks were found in the infrared spectra of these compounds; one is assigned to form I and the other to form II (anticipating the results in the sequel, we have given the approximate wavelength of absorption for each form in eq 1). Rotational isomerism of this type has been reported previously for certain amides,[4a,d] nitrosoamines,[4b] nitrites,[4c] carbamates,[5] esters,[6] ketones,[6b,7] and for still other carbonyl compounds.[8]

The energy barrier leading to two coplanar forms of the nitrocarbamate is provided by the partial double-bond character of the C–N bond in this "amide-like" molecule, a result of resonance (Figure 1).

Cyclic Nitrocarbamates.—Three cyclic nitrocarbamates (III, IV, and V) were also prepared by the nitration of the parent carbamates; each compound showed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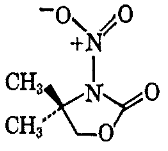
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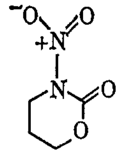
V

only a single carbonyl peak in the infrared. Compounds III and IV have carbonyl bands at about 5.45 μ (1835 cm^{-1}) in CCl_4, and compound V has an absorption band at 5.57 (1795 cm^{-1}) in CCl_4 and at 5.62 μ (1779 cm^{-1}) in $CHCl_3$. This shift to shorter wavelengths of about 0.1 μ in going from a six- to a five-membered ring is known to occur in lactones and cyclic ketones. In the two latter cases, the positions of the carbonyl bands for the six-membered ring compounds are approximately the same as those for the acyclic compounds, and we may assume the same to be true for compound V *vs.* the acyclic compounds with a similar geometry (form II, eq 1). That is, form II with aligned nitro and carbonyl dipoles is assigned the 5.6-μ peak (also found in the cyclic compound V) and form I, with essentially opposed dipoles, is assigned the 5.7-μ peak. This assignment is supported by the following simple argument. In form II, the nitro dipole would be expected to decrease the importance of those resonance contributors which give the carbonyl group single-bond character (Figure 1) and thus the inter-

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[1] Presented, in part, at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 6, 1964, Abstracts, p 2N.

[2] (a) E. H. White and D. W. Grisley, Jr., *J. Am. Chem. Soc.*, **83**, 1191 (1961). (b) Paper II: E. H. White and R. J. Baumgarten, *J. Org. Chem.*, **29**, 3636 (1964).

[3] This conclusion has been strengthened by the finding that the Raman spectrum of methyl N-(*n*-butyl)-N-nitrocarbamate did not show any strong or medium bands, the overtone or combination bands of which would fall in the carbonyl region of the spectrum. We thank Dr. Joseph DiGiorgio for this determination. See also the discussion section of this paper.

[4] W. D. Phillips, "Determination of Organic Structures by Physical Methods," Vol. 2, F. C. Nachod and W. D. Phillips, Ed., Academic Press Inc., New York, N. Y., 1962: (a) Chapter 6, p 441; (b) p 437; (c) p 442. (d) T. H. Siddall, *Tetrahedron Letters*, **No. 18**, 2027 (1966).

[5] C. M. Lee and W. D. Kumler, *J. Am. Chem. Soc.*, **83**, 4596 (1961).

[6] (a) R. N. Jones, P. Humphries, F. Herling, and K. Dobriner, *ibid.*, **73**, 3215 (1951); (b) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 4294 (1957); (c) T. L. Brown, *J. Am. Chem. Soc.*, **80**, 3513 (1958); (d) C. J. W. Brooks, G. Eglinton, and J. F. Norman, *J. Chem. Soc.*, 106 (1961).

[7] R. L. Erskine and E. S. Waight, *ibid.*, 3425 (1960).

[8] S. Mizushima, T. Shimanouchi, I. Ichishima, T. Miyazawa, I. Nakagawa, and T. Araki, *J. Am. Chem. Soc.*, **78**, 2038 (1956).

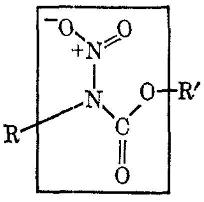
action would lead to a higher carbonyl frequency for form II than for I.[9] These assignments are, furthermore, consistent with the effects of polar solvents and the steric effects to be discussed.

Frequencies of the Carbonyl Bands.—The carbonyl absorptions for compounds I and II–V, illustrating the assignments given in the previous section, are given in Figure 2. The differences in the separation of the two bands are slight, but real; they are presumably related to the size and nature of the R groups in forms I and II, but the relationship is not a simple one. Compound I, IIa absorbs at abnormally high frequencies; the asymmetric nitro stretch and the ultraviolet spectrum were also at abnormally high frequencies indicating some special structural feature. The ionization, tautomerism, and dimerization of this compound were not studied, however, and no attempt will be made to correlate it with the other members of the series.

The Substituent Effect.—The effect of the substituent R on the optical density (OD) ratio of the two carbonyl peaks is given in Figure 3. This ratio

$$\text{OD ratio} = (\text{OD of high-frequency peak})/(\text{OD of low-frequency peak}) \qquad (2)$$

is an approximate measure of the equilibrium constant for the equilibrium as written in eq 1. The trend for the first four members is in a reasonable direction. Because of resonance interactions in the nitrocarbamates (Figure 1), the atoms within the rectangles in VI and VII are in one plane. In form VII, rotation of the R′O group leads to considerable nonbonded interaction between the R and R′ groups, and since R is larger than the NO_2 group, form VI is favored by large R substituents (as found, Figure 3). The triethylcarbinyl compound (I, IIf) gives a point (0.7) that reverses the trend established by the other members of the series. This reversal is probably associated with the bulk of the triethylcarbinyl group and it suggests that the nitro and/or carbomethoxy groups may be tilted out of the molecular plane. Since compounds I, IIe and f give ultraviolet spectra considerably shifted from the spectra of the other compounds (Table IV), it is probable that the point for the *t*-butyl compound (Figure 3) is also high, and that both compounds I, IIe and f are noncoplanar. In addition, we have now found that ethyl N-nitro-N-(dimethylethylcarbinyl)carbamate gives, in accordance with the relative sizes of the R groups, an OD ratio (0.6) between those of compounds I, IIe and f. A quantitative accounting for this increase in the OD ratios is difficult since the extinction coefficients for the planar and nonplanar forms may be quite different, and since noncoplanarity leads to additional isometric forms in this connection, note that the absorption bands are often broad and possibly complex (Figures 7 and 8).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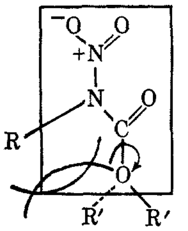
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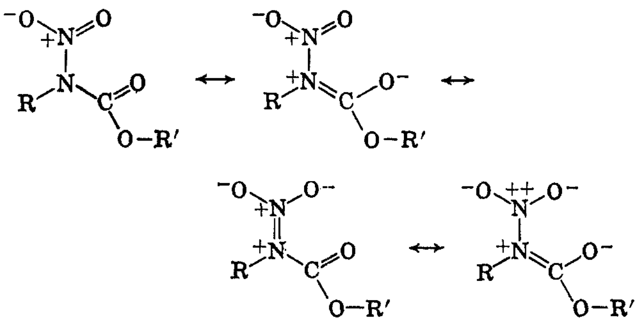
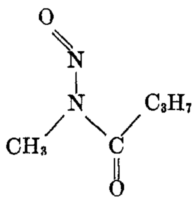
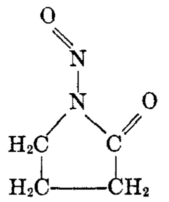


Figure 1.—Principal resonance contributors of the N-nitrocarbamates.

Solvent Effects.—Plots of the optical density ratios of the two carbonyl peaks (eq 2) for compounds I, IIb and e *vs.* the dielectric constant[10] of the solvents used are given in Figure 4 (the solvents were transparent in the region scanned with the exceptions of benzene and carbon disulfide; the ratios in these solvents are, therefore, of lower accuracy). For both compounds, the high-frequency peak (assigned to form II) predominated in the neat liquid and in polar solvents, and the low-frequency peak (assigned to form I) predominated in nonpolar solvents (for compounds I, IIb, form I was also found to predominate in the gas phase). This trend is in the expected direction; form II with essentially parallel nitro and carbonyl dipoles is certainly the more polar of the two forms, and, as such, would be preferentially solvated and stabilized. In a related series, Huisgen and Reimlinger have shown that acyclic N-nitrosoamides, which exist largely in the transoid form (VIII) have low dipole moments (0.92 D. units for compound VIII), whereas N-nitrosopyrrolidone (IX), with aligned nitroso and carbonyl dipoles, has a high dielectric constant (4.58 D.).[11] Other cases in which the more polar form (among rotational isomers) has been shown to be favored by polar solvents may be found in ref 6b–d and 8. The medium affects the carbonyl peaks in yet another way. As shown in Figure 2, both bands are shifted to lower frequencies in polar solvents,[12] with a slightly greater shift apparent for the high-frequency peak of compound I, IIe, *e.g.*, and for the low-frequency peak of compound I, IIc.


VIII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Temperature Effects.—The optical density ratios of the carbonyl peaks (eq 2) are given at several temperatures in Table I. Values were not obtained at higher temperatures because of the thermal in-

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[9] Interpretations of this type have been given in other cases of rotational isomerism.[6b,c,7]

[10] A. A. Maryott and E. A. Smith, Circular 514, National Bureau of Standards, Washington, D. C., 1951.

[11] R. Huisgen and H. Reimlinger, *Ann.*, **599**, 11 (1956).

[12] This is the normal trend: K. Nakanishi in "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p 59.

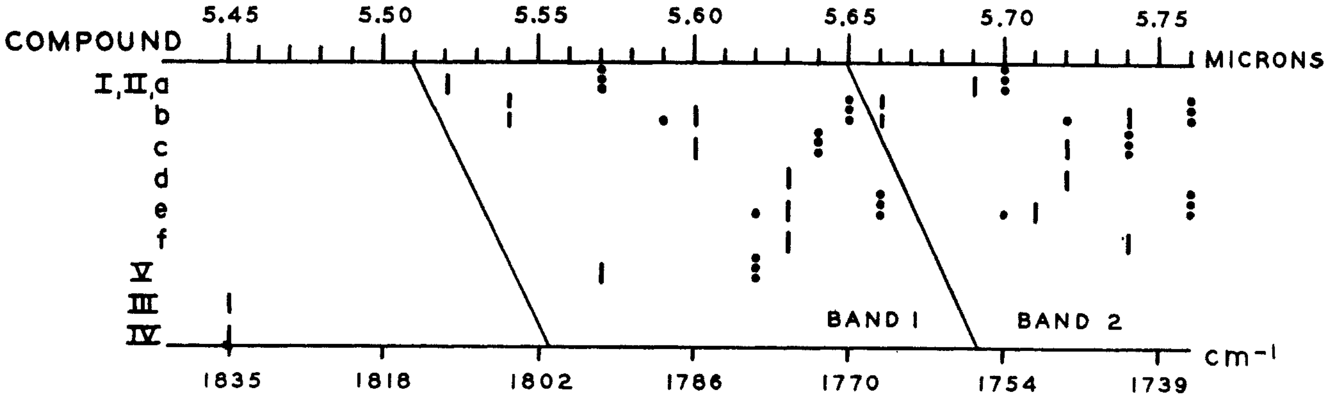

Figure 2.—Carbonyl absorption frequencies of the nitrocarbamates in the infrared (| in CCl_4; ⁝ in $CHCl_3$; · in hexane; and ¦ in the vapor phase).

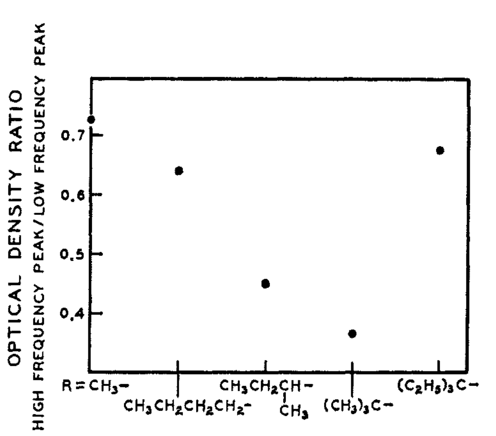

Figure 3.—Effect of R on the optical density ratios of the nitrocarbamates (measured in CCl_4).

Table I

Optical Density Ratios (Eq 2) at Various Temperatures

Compd	Solvent	Temp, °C	OD ratio
I, IIc	Hexane	31	0.74
		−17	0.77
		−51	0.82
I, IIc	CH_2Cl_2	28	2.3
		4	2.6
		−35	3.4
		−52	3.9
I, IIc	None (neat liquid)	30	1.6
		−180	3.1
I, IId	None	30	1.2
		−170	1.5
I, IIe	None	30	1.1
		−125	1.7
I, IIf	None	31	1.2
		−97	2.2

stability of these compounds.[2,13] In all cases, form II (the more polar form) was favored at low temperatures. Since dielectric constants increase in magnitude with a drop in temperature, the observed changes may be another manifestation of the effect of polarity of the solvent. In addition, both peaks were shifted at low temperatures, although the effect was small; the carbonyl peaks for compound I, IIe, for example, appeared at 5.62 and 5.73 μ in a liquid film at 30°, and at 5.63 and 5.76 μ in the supercooled glassy state at −170° (see the Experimental Section for other examples).

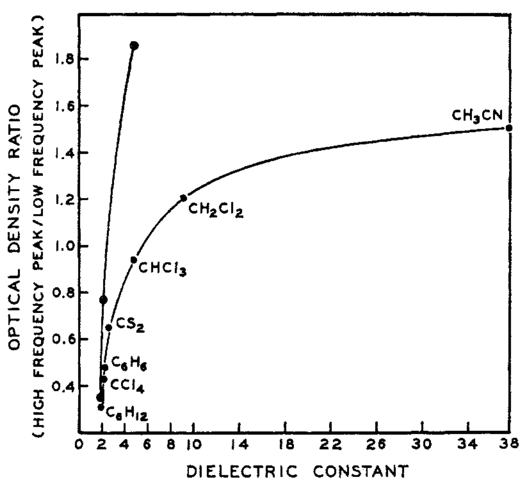

Figure 4.—Effect of solvent polarity on the equilibrium between forms I and II (eq 2) (concn = *ca.* 0.02 *M*; I, IIb = ⊙; I, IIe = ●).

We also noted that at low temperatures, the spectra of compound I, IIc in CH_2Cl_2 and in hexane developed weak peaks at 5.29 and at 5.90 μ.

The carbonyl peaks for I and II are symmetrical in shape and are of approximately the same width; if now we assume that the two forms have approximately the same extinction coefficients, our optical density ratios (eq 2) become the equilibrium constants for the reaction in eq 1. The latter assumption may introduce an error in the equilibrium constants, but it is unlikely to be large;[14] furthermore, if the error is constant over the temperature range studied, the value of $\Delta H°$ calculated from the slope of a plot of log K *vs.* $1/T$ will be independent of this error. A plot of the change in log K with temperature for compound I, IIc in CH_2Cl_2 is given in Figure 5; the calculated value of $\Delta H°$ is −880 cal/mole. In view of the foregoing comments and the fact that the dielectric constant is changing over the wide temperature range used, not much weight can be placed on the value, but it does indicate that the energy difference between the forms is small. Similar plots for the effect of temperature on liquid films of compound I, IIe give values for $\Delta H°$ of

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[13] E. H. White and L. A. Dolak, *J. Am. Chem. Soc.*, **88**, 3790 (1966).

[14] We have observed that the optical density of the carbonyl peak of ethyl acetate is 50% greater than that for N-methyl-N-nitroacetamide. The integrated absorption intensities of various carbonyl compounds cover the range from 2.2 for ethyl acetate through 2.8 for ethyl propionate and 3.1 for acetanilide to 3.8 for methyl carbonate: G. M. Barrow, *J. Chem. Phys.*, **21**, 2008 (1953).

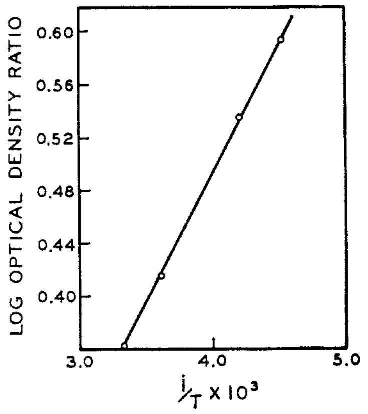

Figure 5.—Effect of temperature on the optical density ratio (eq 2) of compound I, IIc in CH_2Cl_2.

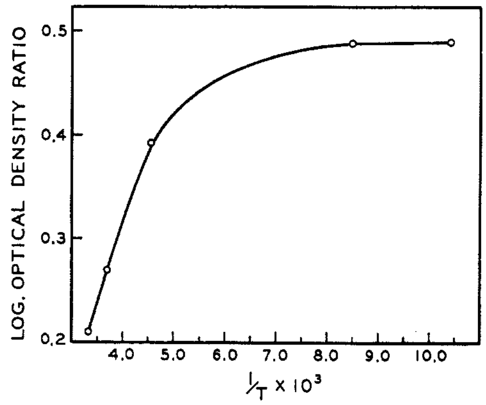

Figure 6.—Optical density ratio (eq 2) of compound I, IIc (neat) as a function of temperature.

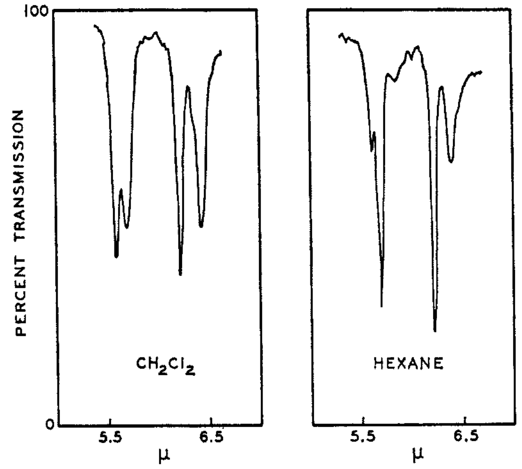

Figure 7.—Solvent effects on the carbonyl and nitro bands of compound I, IIe.

ca. −1 kcal/mole, whereas the corresponding value for the equilibrium measured on solutions in the nonpolar solvent hexane (which has a small change in dielectric constant with temperature) was −170 cal/mole.

When a liquid film of compound I, IIc was rapidly cooled, it was observed that the optical density ratio increased with cooling, but that it remained essentially constant below *ca.* −90° (Figure 6); a similar limiting OD ratio was also obtained when vapors of the compound were trapped out on a sodium chloride window precooled to −185°. We interpret these results to mean that the barrier to rotation in the supercooled liquid is such that rotation of the carbomethoxy group ceases below *ca.* −90°. Similar cut-off points were observed during the cooling of compounds I, IId, e–f.

When the liquid films were allowed to warm up slowly, or when liquid films were cooled slowly, crystallization of the compounds occurred. The infrared spectra of the crystalline forms were considerably simpler than those of the liquid films. Each showed, for example, only a single carbonyl peak; we assume that only a single form (I or II) of these compounds is present in the crystalline phase. It is interesting that form I was present in the crystalline state of compound I, IIe (judging from the carbonyl band in the crystalline state at 5.75 μ), whereas form II was present in the crystalline states of compounds I, IIc, d, and f (with bands in the crystalline state at 5.59, 5.66, and 5.63 μ, respectively). On crystallization, extensive changes also occur in the fingerprint region of the spectrum; examples of these changes may be seen in Figure 8.

Infrared Absorption of the Nitro Group.—The symmetric stretching frequency of the nitro group was not resolved in our compounds. The labeling of compound I, IIc with N^{15} in the nitro group resulted in appreciable changes in the infrared spectrum only at 1580 cm^{-1} (asymmetric stretch) and 751 cm^{-1} (along with slight changes at 1305, 870, and 720 cm^{-1}).[2]

The asymmetric stretch at about 6.3 μ (*ca.* 1580 cm^{-1}) was clearly resolved in all our compounds, however. For compounds I, IIb, c, and d, a single, broad band at 6.2 μ was observed in the spectra of the neat liquids and of solutions in polar solvents, whereas in nonpolar solvents the band was narrower and at slightly shorter wavelengths. Apparently the interactions of the nitro group with the two oxygen atoms of the carbomethoxy group (as in forms I and II) are essentially the same. For compounds I, IIe and f, however, the asymmetric stretch of the nitro group appeared as a doublet, with peaks essentially symmetrically displaced with respect to the single nitro peak of compounds I, IIa–d. Each nitro band is paired with one of the carbonyl bands as shown by simultaneous changes in the inner and outer set of the total of four peaks as the solvent (Figure 7) or temperature (Figure 8) is changed. This effect was turned to advantage in showing that the codeposition of compound I, IIe and a large excess of decane (both from the vapor states) on a liquid nitrogen cooled cold finger (for the infrared studies) yielded a molecular dispersion of I, IIe in the decane, rather than a suspension of crystallites of I, IIe in the decane. That is, the infrared spectrum of I, IIe in a decane matrix prepared in this way at −185° was almost identical with that of a cool, fluid solution of compound I, IIe in hexane (Figure 7) and quite different from the spectrum of the supercooled liquid or the crystalline phase of I, IIe (see Figure 8).

Bands in the Fingerprint Region.—The two carbonyl bands of the nitrocarbamates change in relative intensity as the temperature is changed or the polarity of the medium is changed. It has also been noted that bands in the fingerprint region change at the same time. The bands that increase along with the low-frequency carbonyl band can presumably be assigned

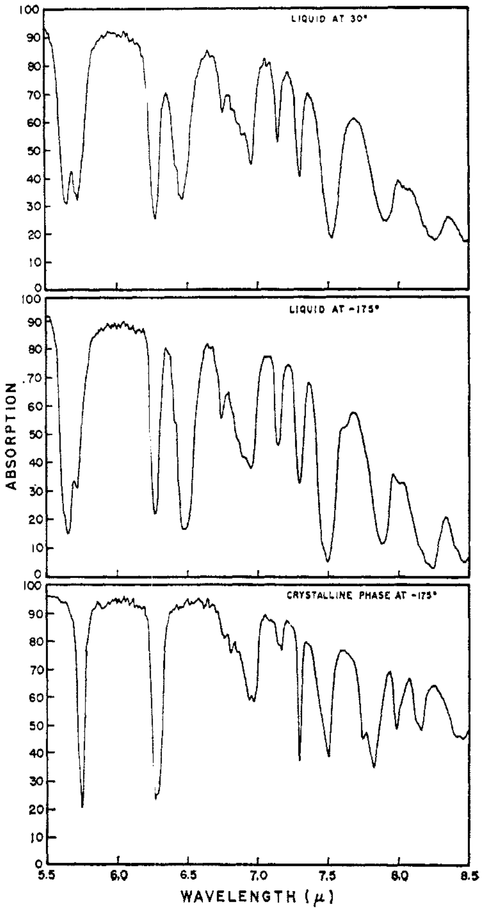

Figure 8.—Infrared spectra of compound I, IIe (Perkin-Elmer Model 21 spectrometer with CaF_2 prism).

to form I and those that correlate with the high-frequency band to form II. A list of these bands is given in Table II. The spectra of the nitrocarbamates contain fewer bands in the crystalline state than in the liquid state, presumably because only a single conformer is present in the crystals (see earlier section). Since some of the bands that remain may be artifacts of some particular polymorphic modification of the crystal, the assignment of these bands to a conformer is less reliable. The infrared spectrum of compound I, IIe in the crystalline state is given in Figure 8; data on the crystalline forms of the other compounds are given in the Experimental Section.

TABLE II

THE ASSIGNMENT OF INFRARED BANDS TO THE CONFORMERS

Compd	Absorption bands, μ	
	Form I	Form II
I, IIc	7.25, 7.43, 8.15, 11.75	7.93, 8.92, 9.86, 13.25, 13.51, 14.90
I, IId	7.42	7.50, 8.35
I, IIf	7.9, 9.75	9.12

Nmr Spectra of the Nitrocarbamates.—The nmr spectra of the nitrocarbamates showed consistent downfield shifts relative to the carbamates (Table III). At low temperatures (−70°), no changes were noted in the spectra of compounds I, IId and e (neat) and I, IIf (in $CDCl_3$) other than slight broadening of the peaks, indicating that essentially free rotation of the R groups occurs at these temperatures even for the very hindered *t*-butyl and triethylcarbinyl groups. The spectrum of compound I, IIf, run on the neat liquid, showed new broad peaks throughout the τ 0–10 range on cooling and pronounced broadening of the old peaks. An opalescence also appears in the liquid at low temperatures and apparently both phenomena are the result of liquid crystal formation.[15]

TABLE III

PROTON NMR SPECTRA OF THE NITROCARBAMATES AND PARENT CARBAMATES[a]

Nitrocarbamate	R	$RN(NO_2)CO_2CH_3$		$RNHCO_2CH_3$	
		τ for R	CO_2CH_3, τ	τ for R	CO_2CH_3, τ
I, IIa	H		6.03		6.28
I, IIb	CH_3	6.38	6.03	7.21 d $J = 3$	6.30
I, IIc	$CH_3CH_2CH_2\mathit{CH}_2$	5.98 t $J = 7$	6.09		6.36
		5.87^c t $J = 6$	6.04^c		
I, IId	$CH_3CH_2CH\mathit{CH}_3$	8.62^c d $J = 6.8$	6.09^c	8.89 d $J = 6.7$	6.39
	$CH_3CH_2\mathit{CH}CH_3$	5.41^c m			
	$CH_3\mathit{CH}_2CHCH_3$	6.09^c m			
	$\mathit{CH}_3CH_2CHCH_3$	9.07^c t $J = 7.5$			
I, IIe	$(CH_3)_3C$	$8.50^{b,c}$	$6.11^{b,c}$	8.70^c	6.42^c
I, IIf	$(CH_3\mathit{CH}_2)_3C$	8.16^b q 8.14^c q $J = 7.4$	$6.10^{b,c}$	8.40 q $J = 7.4$	6.43
	$(\mathit{CH}_3CH_2)_3C$	$9.11^{b,c}$ t $J = 7.4$		9.21 t $J = 7.4$	
V	CH_2NNO_2	5.6^b t $J = 5.5$			

[a] In CCl_4, except as noted; s = singlet, d = doublet, t = triplet, q = quarter, m = multiplet; J in cps. [b] In $CDCl_3$. [c] Neat liquid.

Ultraviolet Spectra of the Nitrocarbamates.—The N-nitrocarbamates have strong absorptions at 230–240 mμ (Table IV), whereas the carbamates them-

TABLE IV

ULTRAVIOLET ABSORPTION BANDS OF THE N-NITROCARBAMATES AND RELATED COMPOUNDS

Compd	Absorptions, mμ			
	λ_{max}	$\epsilon \times 10^{-3}$	λ_{max}	$\epsilon \times 10^{-2}$
	A. In Hexane			
I, IIa	210	7.0	...	...
I, IIb	228	5.9	275–300	2.0
I, IIc	233	5.4	280–300	3.4
I, IId	236	3.8	280–300	3.0
I, IIe	238 sh	1.6	330	0.66
I, IIf	sh	...	338	0.59
XI	239	7.50		
XII	240	6.75		
2-Methyl-2-nitropropane			281	0.22
N-Nitrodiethylamine[a]	241	8.5	358	0.32
	B. In 95% Ethanol			
I, IIa	217	8.5	257	28
I, IIb	232	6.0	275–300	2.6
I, IIc	236	5.1	280–300	3.4
I, IId	239	3.5	280–300	3.4
I, IIe	235	2.0	330	0.5
I, IIf	238	2.9	335	0.44
V	233	5.77	280–300	1.9
III	227	5.3	280–300	0.92
IV	228	4.2	280–300	1.5

[a] In CH_2Cl_2.

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[15] We thank Dr. John D. Baldeschwieler for this interpretation of the nmr spectrum.

selves are transparent in the accessible region of the ultraviolet. Our values agree with those of related compounds reported by Curry and Mason,[16] and they confirm the finding of Curry and Mason that nitrocarbamates with large R groups have considerably reduced absorption coefficients. In addition to the $\pi-\pi^*$ absorptions, weak, broad bands appear at longer wavelengths (Table IV) which can be assigned to $n-\pi^*$ transitions.[17] Compounds I, IIb–d and III, IV, and V have $n-\pi^*$ bands at *ca.* 280 mμ, whereas compounds I, IIe and f have these bands displaced to longer wavelengths (*ca.* 330 mμ). The $\pi-\pi^*$ bands for compounds I, IIe and f are also unusual in that they appear as shoulders on intense bands at shorter wavelengths; it should also be pointed out that these two compounds were the only nitrocarbamates to have split absorption bands for the asymmetric stretching mode of the nitro group. The 330-mμ peak of compound I, IIe was examined at $-60°$ in ethanol, but no change was apparent with the exception of the appearance of some weak, fine structure in the band.

Discussion.—Although it is not possible to rule out Fermi resonance absolutely as a cause of splitting of the carbonyl bands, a number of our results support strongly the interpretation that rotational isomerism is responsible.[18] (a) The N^{14} and N^{15} nitrocarbamates (labeled in the nitro group) show the same splitting pattern. (b) Large changes occur in the fingerprint region of the infrared spectra parallel with changes in the carbonyl region. (c) In two compounds (I, IIe and f changes occur in a doublet assigned to the asymmetric nitro stretch in concert with changes in the carbonyl bands. (d) The crystalline compounds show only a single carbonyl peak (not at an averaged position, but at one of the positions in the split peak), a single nitro peak, and a simpler spectrum in the fingerprint region. (e) Either carbonyl peak can be made the more intense, depending on the solvent and temperature. (f) The effect of structural changes on the carbonyl bands (in cyclic compounds, nitroamides, and nitrosocarbamates) can be interpreted without exception in terms of rotational isomerism. (g) The solvent shifts do not follow the pattern of those in which Fermi resonance is involved.[2a,6d]

On the basis of rotational isomerism, the spectra of compounds I, IIb–d are readily interpreted. The spectra of compounds I, IIe and f require additional comment, on the other hand, since they show two bands for the asymmetric nitro stretching mode in the infrared. Fortunately, the two carbonyl bands and the two bands of the nitro group are coupled (Figure 7), a fact that indicates that here, just as with compound I, IIb–d, two forms of the nitrocarbamate are involved. In the two forms for compounds I, IIb–d, we assume that the interactions of the nitro group with the two different oxygen atoms of the carbomethoxy group (eq 1) are approximately the same, chiefly as a result of the large distance between these groups. Compounds IIe and f possess bulky R groups, and the doubling of the nitro bands is presumably a consequence of this. A molecular model of compound I, IIe shows serious, nonbonded interactions between the R, NO_2, and CO_2CH_3 groups in the coplanar form. These interactions could be relieved by bond bending, bond stretching, and by a twisting of the NO_2 or CO_2CH_3 groups out of the molecular plane. Bond stretching is less favorable energetically than bond bending (valence angle deformation),[19] and in any case, it is not obvious how a lengthening of bonds could account for the doubling of the number of absorption bands. The distortion of the R-N-NO_2 and R-N-CO_2CH_3 bond angles by large R groups could in principle lead to a greater interaction between the NO_2 and CO_2CH_3 groupings. At close approaches, the interaction of the nitro group with the carbonyl oxygen might be different from the interaction with the ether oxygen, and this difference might result in different infrared frequencies for the asymmetric stretching modes of the nitro groups in forms I and II (eq 1). It seems probable, in addition, that the nitro and carbomethoxy groups are tilted somewhat out of the molecular plane by large R groups (Figure 9; the tilting of the nitro group was not shown in order to simplify the drawing). This process would occur at the expense of resonance energy, but in related cases, it has been shown that the resonance energy is little affected by small changes in the angle of rotation.[20] In the tilted form shown in Figure 9, there is the possibility of interaction of the unshared electrons on the nitro group with the π orbitals of the carbonyl group (reaching a maximum at an angle of rotation of 90°). Interactions of this type[21] have been invoked previously to account for bathochromic shifts in the infrared spectra of compounds such as X.[21b] This extra interaction together with the proximity effect may thus be responsible for the clear differentiation of the nitro groups in forms I and IIe, f (as reflected in the infrared spectra).

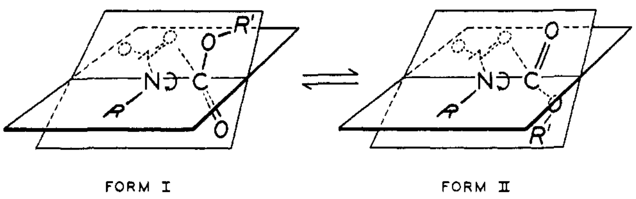
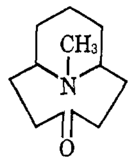


Figure 9.—"Tilted" forms of compounds I, IIe and f.



X

The ultraviolet data (Table IV) support the contention that the nitrocarbamates with bulky substituents are not planar molecules. Compounds I, IIb and c have spectra similar to that of the cyclic analog V, and it seems a safe assumption that they have planar structures, and that forms I and II have essentially the same ultraviolet spectra. In contrast, the $n-\pi^*$ transi-

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[16] H. M. Curry and J. Mason, *J. Am. Chem. Soc.*, **73**, 5449 (1951).

[17] J. W. Sidman, *Chem. Rev.*, **58**, 689 (1958).

[18] See also footnotes 3 and 2a.

[19] F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956.

[20] H. H. Jaffe and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962.

[21] (a) F. A. L. Anet, A. S. Bailey, and R. Robinson, *Chem. Ind.* (London), 944 (1953); (b) N. J. Leonard, D. E. Morrow, and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 5476 (1957); (c) E. W. Warnhoff and W. C. Wildman, *ibid.*, **82**, 1472 (1960).

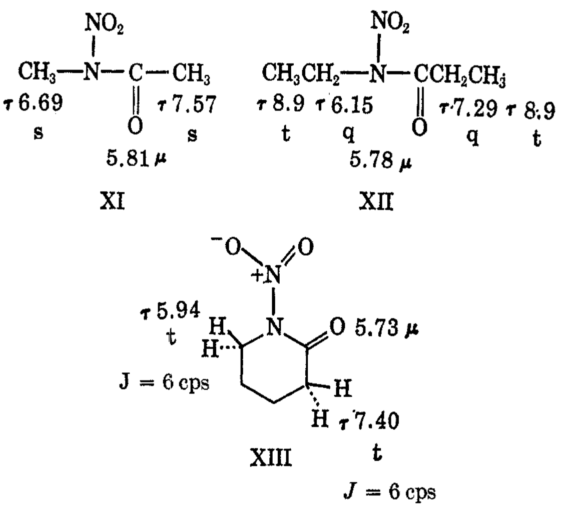


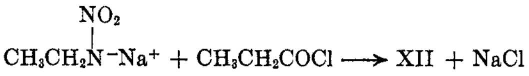
Figure 10.—Infrared and nmr data for the N-nitroamides (infrared was taken in CCl_4, 0.5-mm cell; nmr was taken in CCl_4; for s, d, t, etc., see footnote *a* in Table III).

tions of compounds I, IIe and f are shifted to longer wavelengths and the extinction coefficients of both bands in the spectra are lower. Decreases in the extinction coefficients for π–π^* transitions have been found for nitro and aminobenzenes substituted in the *ortho* positions by large R groups.[22] As an example, nitromestylene in hexane has a band at 253 mμ (ϵ 3600) and one at 335 mμ (ϵ 630), whereas *p*-nitrotoluene has a low wavelength band at 265 mμ with an extinction coefficient of 13,600 and no readily detectible band at longer wave lengths. This decrease in absorption intensity of the π–π^* band is usually attributed to a twisting of the nitro group out of the molecular plane.[16,22] Murrell has proposed that this twisting, at least in the benzene series, should also lead to intense n–π^* transitions.[23] This effect is apparent in the nitromesitylene–nitrotoluene case cited above, but it is not apparent in our data. Actually, a correction should be made for the extinction of the bands of the nitrocarbamates at 280 mμ since the intense bands at 230–240 mμ have tails that extend to this region. Even with a liberal allowance for this factor, however, the n–π^* absorptions for compounds I, IIb–d appear to be about twice as intense as those for compounds I, IIe and f. Our data suggest that compounds I, IIe and f are nonplanar, but because of the flexibility of the molecules, the geometry cannot be defined at this time.

Infrared spectra of model compounds in CCl_4 have not helped in the interpretation of the spectra of the nitrocarbamates. Methyl *o*-nitrobenzoate shows a nitro band at 6.49 and a single carbonyl band at 5.73 μ; presumably a single, nonplanar form is present. The spectrum of the *para* isomer, with bands at 5.75 and 6.50 μ is surprisingly similar. Differences between *p*-nitrotoluene (6.23 μ) and nitromesitylene (6.21 μ) are also small. Strong conjugation does have an effect on the absorption wavelength of the nitro group, however, as shown by the fact that the asymmetric stretching mode for N-nitrodiethylamine is found at 6.65, compared with 6.45 μ for 2-nitropropane.

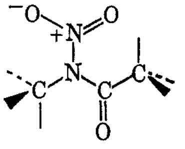
N-Nitroamides

Two N-nitroamides, N-methyl-N-nitroacetamide (XI) and N-nitrovalerolactam (XIII), were prepared by nitration of the corresponding amides. By-products were often formed in the direct nitration, however (in particular, nitrate esters[2b]), and compound XII, N-ethyl-N-nitropropionamide, was prepared instead by the acylation of the sodium salt of N-nitroethylamine.[2]

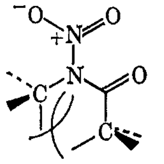


$$CH_3CH_2\overset{NO_2}{\overset{|}{N}}{}^-Na^+ + CH_3CH_2COCl \longrightarrow XII + NaCl$$

The N-nitroamides have only one band in the carbonyl region of the infrared and almost certainly, because of the large size of alkyl groups relative to oxygen,[24] they exist largely in conformation XIV.



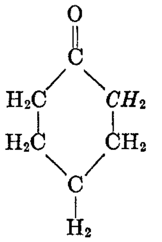
XIV



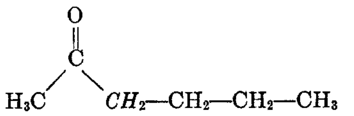
XV

The carbonyl frequencies and nmr bands for the three nitroamides are given in Figure 10. As expected, the carbonyl band for the cyclic nitroamide (XIII, with geometry XV) was at a shorter wavelength than the carbonyl bands for the acyclic compounds. The reasons for the shift are presumably those outlined in the section on the nitrocarbamates.

It was hoped that support for conformation XIV for the acyclic nitroamides would be provided by the nmr spectra. In the cyclic compound XIII, the methylenic hydrogens α to the carbonyl group are well away from the deshielding range of the nitro group whereas in conformation XIV of the acyclic compounds (but not in XV) they are near the nitro group. The band position for the α-methylenic group in compound XIII is at τ 7.40, whereas that for the α-methylenic hydrogens of compound XII is at τ 7.29. The difference between these values is very nearly the same as that between cyclohexanone (XVI) and methyl butyl ketone (XVII) and as a result, our nmr spectra are of no assistance in this matter.



XVI, τ 7.68



XVII, τ 7.55

Experimental Section

Infrared spectra were taken on a Perkin-Elmer Infracord (Model 337) or on a Perkin-Elmer Model 21 fitted with either CaF_2 or NaCl prisms. The frequencies were calibrated against atmospheric bands or a polystyrene film. Solutions were usually run at 0.02 *M* in 0.5-mm cells. The optical densities (log I_0/I)

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[22] W. R. Remington, *J. Am. Chem. Soc.*, **67**, 1838 (1945).

[23] J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," John Wiley and Sons, Inc., New York, N. Y., 1963, p 187.

[24] L. A. LaPlanche and M. T. Rogers, *J. Am. Chem. Soc.*, **85**, 3728 (1963).

were calculated from the peak heights, and values were kept near 0.03.[25] The low-temperature runs were made in cells of special design. The ultraviolet spectra were taken on a Beckman spectrophotometer (Model DK-2) and on a Cary spectrophotometer (Model 14). The nmr spectra were taken on a Varian spectrophotometer (Model A-60).

The Methyl Carbamates.—The N-methyl, *n*-butyl, *sec*-butyl, and *t*-butyl derivatives of methyl carbamate were prepared from the amines and methyl chloroformate by standard literature procedures.

Triethylcarbinylamine.—This compound was prepared by applying the Ritter reaction[26] to triethylcarbinol. To a mixture of the carbinol (35 g, 0.3 mole) and acetic acid (35 ml) was added sodium cyanide (15 g, 0.3 mole). With ice-bath cooling, a mixture of sulfuric acid (70 g) and acetic acid (30 ml) was added dropwise with vigorous stirring. The mixture was allowed to reach room temperature slowly by allowing the ice to melt overnight. The temperature was then raised to 65° for 2 hr. Sodium hydroxide was then added (500 ml of a 25% solution) and the alkaline mixture was refluxed with stirring overnight. The amine was then steam distilled from the reaction mixture, dried, and distilled at 38° (17 mm) (lit.[27] 133°). The yield was 18.7 g (0.16 mole, 54%), n^{24}_{D} 1.4251.

N-Triethylcarbinylformamide.—This compound was isolated from the reaction mixture above (before hydrolysis) by making the acidic mixture only slightly basic and extracting it with ether. After evaporation, the product was recrystallized from hexane and sublimed. The compound melted at 52.2–53.5° and the yield was about 75%.

Anal. Calcd for $C_8H_{17}NO$: C, 67.09; H, 11.96; N, 9.78. Found: C, 67.17; H, 12.14; N, 9.47.

Methyl N-(Triethylcarbinyl)carbamate.—This carbamate was prepared through the addition of methyl chloroformate (7.5 g, 0.08 mole) to an ice-cooled solution of triethylcarbinylamine (8.5 g, 0.07 mole) in sodium hydroxide (50 ml of a 10% solution) in such a way that the temperature never exceeded 15°. The mixture was extracted with ether, and the ether was dried with sodium sulfate and then evaporated. The residue, crystallized from methanol and dried *in vacuo* overnight, melted at 59.5–61.5°. The yield was usually about 61%.

Anal. Calcd for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.09. Found: C, 62.59; H, 11.07; N, 8.27.

Methyl N-Nitrocarbamate (I, IIa).—This compound was prepared from the carbamate and ethyl nitrate according to the directions of Thiele,[28] mp 85.8–87.6° (lit.[28] mp 88°). The infrared spectrum of this compound in CCl_4 showed a sharp peak in the nonhydrogen-bonded region (2.74 μ).

Methyl N-Nitro-N-methylcarbamate (I, IIb).—This nitrocarbamate was prepared through the addition of methyl N-methylcarbamate (5 g, 0.005 mole) to a mixture of cold acetic acid (50 ml) and fuming nitric acid (20 g). The ice bath was removed and the mixture was allowed to reach room temperature, then poured into an equal volume of water. This solution was extracted with ether, and the ether solution was washed with carbonate solution until neutral. The ether was dried over sodium sulfate and evaporated at aspirator pressure and room temperature. The residue was distilled at 38° (1 μ) with a bath temperature of 78° [lit.[29] bp 93° (15 mm)] to yield 2.0 g (0.015 mole, 27%) of a clear oil, n^{25}_{D} 1.4559.

Methyl N-Nitro-N-(*n*-butyl)carbamate (I, IIc).—This compound was obtained in a procedure similar to that used for I, IIb. Obtained was 77% of a clear oil, bp 32° (0.1 mm), n^{27}_{D} 1.4449 (lit.[30] n^{22}_{D} 1.4486).

Anal. Calcd for $C_6H_{12}N_2O_4$: C, 40.90; H, 6.82. Found: C, 41.06; H, 6.98.

Methyl N-Nitro-N-(*sec*-butyl)carbamate (I, IId).—This compound was prepared in a manner similar to that used for compound I, IIb. Obtained was 51% of a clear oil, bp 27° (0.05 mm), n^{25}_{D} 1.4393 (lit.[30] $n^{23.3}_{\mathrm{D}}$ 1.4417).

Methyl N-Nitro-N-(*t*-butyl)carbamate (I, IIe).—This compound was prepared in a manner similar to that used for compound I, IIb. Obtained was 78% of a clear oil, bp 32° (0.1 mm), n^{25}_{D} 1.4342.

Anal. Calcd for $C_6H_{12}N_2O_4$: C, 40.90; H, 6.82. Found: C, 41.08; H, 6.49.

Methyl N-Nitro-N-(triethylcarbinyl)carbamate (I, IIf).—This compound was difficult to prepare because of its instability and the general difficulty of nitrating hindered carbamates and amides. In a typical run, the carbamate (6.4 g, 0.037 mole) was added to a mixture of 12 g of acetic anhydride and 8 g of 100% nitric acid at 0°. When the ice bath was removed, the mixture slowly warmed to room temperature and at about 24° spontaneous bubbling commenced. After another 15 min the mixture had turned a darker shade of yellow, bubbling had increased, and the temperature rose to about 32°. If this temperature was exceeded, the reaction became very vigorous and an impurity showed up in the product with a strong band in the infrared at 6.1 μ (probably a nitrate ester[3]). A lower temperaatures, considerable starting material was recovered. The mixture was then poured into 100 ml of ice–water and extracted with ether. The ether solution was neutralized with sodium carbonate, dried over sodium sulfate, and evaporated at room temperature. The residue at this point usually weighed about 6.0 g and its was relatively free of the nitrate. The nitrocarbamate could be slowly concentrated by crystallizing the residue repeatedly from hexane at −50° and decanting the solution enriched in the nitrocarbamate. Evaporation of the hexane and distillation of the resulting oil at room temperature (10^{-5} mm) yielded as pure a sample of the nitrocarbamate as we were able to prepare. (Chromatography on silica gel and alumina led to decomposition of the nitrocarbamate.)

Anal. Calcd for $C_9H_{18}N_2O_4$: C, 49.53; H, 8.31; N, 12.84. Found: C, 50.32; H, 8.41; N, 11.90.

1,3-Oxazolidinone-2.[31]—This compound was prepared according to the general method of Caldwell.[32] To a mixture of ethyl carbonate (23.6 g, 0.2 mole) and 2-aminoethanol (12.2 g, 0.2 mole) was added a small piece of sodium. When the sodium dissolved on stirring, the mixture began to reflux and the apparatus was arranged for distillation. A total of 21 ml of ethanol was collected (90% yield). The pot residue solidified on cooling and the product was recrystallized from ethanol to yield 7.0 g (0.08 mole, 40% of the oxazolidinone), mp 88.0–90.0° (lit.[33] mp 90°).

N-Nitro-1,3-oxazolidinone-2 (III).—This compound was obtained essentially by the method of Franchimont.[34] 2-Oxazolidone (2 g, 0.23 mole) was dissolved in a fourfold excess of fuming nitric acid and the solution was evaporated to dryness on a steam bath. The product solidified on cooling; it was dried *in vacuo* overnight, and recrystallized from benzene to give 1.6 g (0.12 mole, 53%) of crystals, mp 108–109.5° (lit.[34] mp 111°).

4,4-Dimethyl-1,3-oxazolidinone-2.—This compound was obtained by refluxing ethyl carbonate (23.6 g, 0.2 mole) and 2-amino-2-methylpropanol (17.8 g, 0.41 mole) (containing a small piece of sodium) for 2 hr. The mixture was then distilled, and the fraction distilling at 118–123° (0.35 mm) [lit.[35] bp 152° (10 mm)] was collected. It crystallized at room temperature to yield 12.7 g (0.14 mole, 73%) of white crystals, mp 55–56° (lit.[36] mp 56.5–58°).

N-Nitro-4,4-dimethyl-1,3-oxazolidinone-2 (IV).—4,4-Dimethyl-1,3-oxazolidone-2 (5 g, 0.045 mole) was added to a mixture of 10 g of fuming nitric acid in 25 ml of acetic anhydride with cooling. Crystals separated from the reaction mixture and the addition of water precipitated the remainder. Filtration, washing with water, and drying yielded 4.5 g of crystals (0.028 mole, 63%). Recrystallization from methanol yielded a material with mp 121–122° (lit.[37] mp 124°).

Tetrahydro-2-hydro-1,3-oxazin-2-one.—3-Aminopropanol (5 g, 0.07 mole) and ethyl carbonate (7.9 g, 0.07 mole) and a small piece of sodium were mixed. After the sodium dissolved completely, the mixture was refluxed for 1 day and then heated to 70° to remove the volatiles. The pot residue (which solidified on cooling) was distilled. The fraction distilling at 123–126° (0.12 mm) was collected and crystallized from ethyl acetate

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(25) J. Powling and H. J. Bernstein, *J. Am. Chem. Soc.*, **73**, 1815 (1951).

(26) J. J. Ritter, *ibid.*, **70**, 4048 (1948).

(27) G. Vexlearschi, *Compt. Rend.*, **228**, 1655 (1949).

(28) J. Thiele, *Ann.*, **302**, 249 (1898).

(29) H. J. Backer, *Rec. Trav. Chim.*, **31**, 190 (1912).

(30) J. W. Bruhl, *Z. Physik. Chem.*, **22**, 390 (1897).

(31) We wish to thank Mr. Filipe Lebron for the preparation of these compounds.

(32) J. R. Caldwell, U. S. Patent 2,656,328 (1953); *Chem. Abstr.*, **48**, 2416*a* (1954).

(33) S. Gabriel, *Ber.*, **21**, 568 (1888).

(34) A. P. N. Franchimont, *Rec. Trav. Chim.*, **21**, 49 (1902).

(35) E. Katchalski and D. B. Ishai, *J. Org. Chem.*, **15**, 1067 (1950).

(36) W. J. Close, *J. Am. Chem. Soc.*, **73**, 95 (1951).

(37) R. B. Carlin and S. A. Heininger, *ibid.*, **77**, 2277 (1955).

to yield white needles (1.4 g, 0.014 mole, 21%) mp 78–90° (lit.[38] mp 77°).

Anal. Calcd for $C_4H_7NO_2$: C, 47.52; H, 6.98; N, 13.85. Found: C, 47.50; H, 6.93; N, 13.96.

Tetrahydro-2-hydro-3-nitro-1,3-oxazin-2-one (V).—A mixture of acetic anhydride (4 g) and fuming nitric acid (2 g) was prepared and to it was added the oxazine (1.0 g, 9.9 moles) at room temperature. The temperature rose to 40° and the solution was cooled and stirred for 1 hr after the addition. The reaction mixture was poured into ice–water and extracted with CH_2Cl_2, and the organic layer was dried and evaporated. Recrystallization of the resulting solid from CCl_4 gave 1.25 g of white crystals (8.6 moles, 87%), mp 75.8–76.3° (lit.[34] mp 74°).

N-Methyl-N-nitroacetamide (XI).—This nitroamide could not be prepared with the nitric acid–acetic anhydride system used for the carbamates. The general method of Runge and Treibs[39] was used instead. N-Methylacetamide (9.0 g, 0.12 mole) was added to a solution of N_2O_5 (12.3 g, 0.11 mole) in 50 ml of $CHCl_3$ at −75°. The mixture was allowed to reach room temperature with stirring, then it was washed with water saturated with salt at 0°. The organic layer was dried with sodium sulfate and evaporated. The residual liquid was distilled at room temperature at *ca.* 1 mm using a spiral column 75 cm in length with an outside diameter of 9 mm. A colorless liquid (4.7 g, 0.04 mole, 39%) was obtained, $n^{26}\text{D}$ 1.4656.

Anal. Calcd for $C_3H_6N_2O_3$: C, 30.51; H, 5.12; N, 23.72. Found: C, 30.65; H, 5.24; N, 23.55.

Some of the more volatile fractions in the distillation contained an impurity (probably a nitrate ester)[2] with a band in the infrared at 6.1 μ.

N-Ethyl-N-nitropropionamide (XII).—This compound was prepared through the addition of the sodium salt of N-nitroethylamine (14.4 g, 0.13 mole) at 25° to a stirred mixture of propionyl chloride (9.3 g, 0.10 mole) and potassium carbonate (10.0 g) in 500 ml of dry acetone. The temperature rose to 50° and then dropped slowly. After a total of 1 hr of stirring, water was added, the mixture was extracted with ether, and the organic layer was dried over magnesium sulfate and then evaporated. The product at this point always contained varying amounts of propionic anhydride as shown by a band in the infrared at 5.5 μ. The mixture was separated in a wire spiral column. The fraction distilling at 38–40° (1 mm) represented pure nitroamide; it weighed 3 g (0.02 mole, 20%), $n^{26}\text{D}$ 1.4538.

Anal. Calcd for $C_5H_{10}N_2O_3$: C, 41.09; H, 6.90; N, 19.17. Found: C, 41.44; H, 7.00; N, 19.07.

In a similar fashion, N-isobutyl-N-nitropropionamide (infrared CO at 5.80 μ in CCl_4, $n^{26}\text{D}$ 1.4478) was prepared from the corresponding nitroamine salt; although the infrared and nmr spectra appeared correct, the material could not be obtained analytically pure.

N-Nitro-δ-valerolactam (XIII).—This compound was prepared by the method used for N-methyl-N-nitroacetamide. The very viscous liquid obtained was distilled at 70° (10^{-5} mm) and then crystallized from ether–hexane mixtures at −35°. Sublimation yielded a colorless solid melting at 29.5–32.5°. This compound had been prepared in an impure state by Runge and Treibs.[39]

Anal. Calcd for $C_5H_8N_2O_3$: C, 41.66; H, 5.59; N, 19.44. Found: C, 41.87; H, 5.98; N, 19.44.

Miscellaneous Infrared Absorptions. A. Infrared Absorption of the Nitro Group.—The following band positions refer to the asymmetric nitro stretch found for various compounds. Listed in each case are the compound number, solvent, and position in μ: (I, IIa) CCl_4, 6.14; $CHCl_3$, 6.15; CS_2, 6.16; CH_3CN, 6.18; (I, IIb) gas phase, 6.17; hexane, 6.26; $CHCl_3$, 6.33; neat, 6.34; (I, IIc) hexane, 6.30; neat, 6.33; crystalline state at −75°, 6.39; liquid at −175°, 6.37; (I, IId) neat, 6.35; crystalline at −50°, 6.37; (I, IIe) hexane, 6.24 + 6.40; CH_2Cl_2, 6.24 + 6.45; neat, 6.27 + 6.45; liquid at −125°, 6.27 + 6.47; crystalline state at −60°, 6.27 (+6.29?); (I, IIf) CCl_4, 6.25 + 6.46; $CHCl_3$ *and* neat, 6.25 + 6.51; liquid at −170°, 6.22 + 6.52; crystalline state at −30°, 6.54; (IV) CCl_4, 6.30; (V) CCl_4, 6.28; $CHCl_3$, 6.29; (XI) neat, 6.34; (XII) neat, 6.40; (XIII) molten at 50°, 6.39.

B. Carbonyl Absorptions of the Nitrocarbamates at Low Temperatures and in the Crystalline State.—Listed in each case is the compound number, phase, temperature, and position in μ: (I, IIc) liquid, 30°, 5.62 + 5.73; supercooled liquid, −175°, 5.63 + 5.76; crystalline, −30°, 5.59; (I, IId) liquid, 30°, 5.66 + 5.73; supercooled liquid, −175°, 5.65 + 5.73; crystalline, −48°, 5.67; (I, IIe) liquid, 30°, 5.63 + 5.71; supercooled liquid, −125°, 5.65 + 5.72; crystalline, −60°, 5.75.

C. Other Bands in the Crystalline State.—Listed are the compound numbers, band positions in μ and a + or − to indicate the new intensity relative to that in the neat liquid: (I, IIc) 7.61 (+), 7.85 (+), 7.92 (−), 8.09 (−), 9.39 (+), 9.70 (−), 14.7 (+); (I, IId) 7.42 (−), 7.50 (+), 8.35 (+); (I, IIf) 7.90 (−), 8.48 (−), 8.70 (−), 9.75 (−), 13.4 (−). See Figure 10 for compound I, IIe.

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