Anal. Calcd for $C_5H_{12}ClNO_2S$: C, 32.35; H, 6.52; Cl, 19.09. Found: C, 32.30; H, 6.31; Cl, 19.3.

N-Methyl-γ-chlorobutanesulfonamide.—3-Chlorobutanesulfonyl chloride (19.1 g, 0.1 mol) was added with stirring to a 30% aqueous solution of methylamine (24 g) at 5°. The yellow oil that separated was treated as described for N-methyl-δ-chlorobutanesulfonamide. Distillation of the residue obtained by evaporation of the solvent afforded N-methyl-γ-chlorobutanesulfonamide (11.1 g): bp 134–135° (0.1 mm); nmr in $CDCl_3$ τ 5.45 (singlet, 1 H), 5.85 (multiplet, 1 H), 6.80 (triplet, 2 H), 7.20 (doublet, 3 H), 7.80 (multiplet, 2 H), 8.43 (doublet, 3 H).

Anal. Calcd for $C_5H_{12}ClNO_2S$: C, 32.35; H, 6.52; Cl, 19.09. Found: C, 32.15; H, 6.41; Cl, 18.8.

Isolation of the Rearranged Products from the Reaction Mixture. Isolation of N-*t*-Butyl-*n*-butanesulfonamide.—The viscous liquid obtained in the photorearrangement was distilled under reduced pressure and a fraction of bp 120–122° (2 mm) was obtained. The ir and nmr spectra of this fraction were the same as those of known N-*t*-butyl-*n*-butanesulfonamide.

Isolation of N-*t*-Butyl-γ-chlorobutanesulfonamide.—A white precipitate was obtained when petroleum ether was added to the viscous liquid (9.0 g) obtained in the photorearrangement. The precipitate was collected by filtration and washed with cold light petroleum ether and then recrystallized from petroleum ether solution (yield 3.8 g), mp 63.0°, not depressed by mixture with the authentic compound. The ir and nmr spectra of this compound were the same as those of authentic N-*t*-butyl-γ-chlorobutanesulfonamide.

Isolation of pure N-*t*-butyl-δ-chlorobutanesulfonamide was unsuccessful because of its low initial content and the small difference in solubility in petroleum ether between γ- and δ-chlorobutanesulfonamides.

Isolation of N-*t*-Butyl-δ-chloropentanesulfonamide.—By adding petroleum ether to the reaction product (32.6 g; Cl ,13.1%) obtained from N-*t*-butyl-N-chloro-*n*-pentanesulfonamide (35.0 g), a white precipitate was obtained. This precipitate was collected by filtration, washed with cold petroleum ether, and recrystallized from petroleum ether. The white crystals (11 g), mp 59°, were identified as N-*t*-butyl-δ-chloropentanesulfonamide (IIIc) by the infrared and nmr spectra and elemental analysis. Characteristic infrared bands appeared at 3380, 2960, 1320, 1140, and 1020 cm^{-1}; nmr (in CCl_4) bands were at τ 4.70 (1 H), 6.00 (multiplet 1 H), 6.90 (triplet, 2 H), 8.15 (multiplet, 4 H), 8.50 (doublet, 3 H), and 8.60 (singlet, 9 H).

Anal. Calcd for $C_9H_{20}ClNO_2S$: C, 44.71; H, 8.34; Cl, 14.24. Found: C, 44.36; H, 8.36; Cl, 14.5.

Isolation of N-*t*-Butyl-γ-chloropentanesulfonamide.—The filtrate (10.0 g) obtained by the treatment described above was passed through an active alumina column and eluted with carbon tetrachloride. N-*t*-Butyl-γ-chloropentanesulfonamide (3.0 g) was isolated as a white crystal and purified by recrystallization from the petroleum ether solution, mp 42°. Characteristic infrared bands appeared at 3380, 2960, 1320, and 1140 cm^{-1}; nmr (in $CDCl_3$) bands were at τ 5.70 (1 H), 6.00 (multiplet, 1 H), 6.72 (triplet, 2 H), 7.83 (multiplet, 2 H), 8.30 (multiplet, 2 H), 8.60 (singlet, 9 H), 8.93 (triplet, 3 H).

Anal. Calcd for $C_9H_{20}ClNO_2S$: C, 44.71; H, 8.34; N, 5.79; Cl, 14.24. Found: C, 44.52; H, 8.51; N, 5.68; Cl, 14.3.

Isolation of N-*t*-Butyl-3-ethylpropanesultam.—The viscous liquid (24 g) obtained in the photoirradiation of N-chloro-N-*t*-butyl-*n*-pentanesulfonamide was dissolved in ethanol. Potassium hydroxide (6 g) was added, and the solution was refluxed for 3 hr. The salt that formed was filtered off, and the ethanol was evaporated. The residue (19 g) was dissolved in ether (50 ml), and the ether solution was extracted with water (50 ml). After evaporation of water, a yellow liquid (2 g) was obtained from the aqueous layer. This product was found to be almost pure by glpc, but it was further refined on a silica gel column. Characteristic infrared bands appeared at 2960, 1300, 1220, and 1135 cm^{-1}; nmr (in $CDCl_3$) bands were at τ 6.60 (multiplet, 1 H), 6.90 (triplet, 2 H), 7.80 (multiplet, 2 H), 8.40 (multiplet, 2 H), 8.60 (singlet, 9 H), and 9.10 (triplet, 3 H).

Anal. Calcd for $C_9H_{19}NO_2S$: C, 52.66; H, 9.33. Found: C, 53.06; H, 9.63.

Registry No.—Ia, 16339-81-4; Ib, 16867-16-6; Ic, 16867-17-7; IIa, 16339-82-5; IIb, 16867-19-9; IIc, 16867-20-2; IIIa, 16339-83-6; IIIb, 16867-22-4; IIIc, 16867-23-5; IVa, 16867-24-6; IVb, 16867-25-7; IVc, 16867-26-8; VII, 16867-27-9.

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Steric Enhancement of Resonance. IV. Absorption Spectra of N-Alkyl- and N,N-Dialkylpicramides

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Spectral displacements on N-alkylation and N,N-dialkylation of picramide are discussed in terms of inductive and steric effects. The phenomenon, *steric enhancement of resonance*, is considered to operate in this series.

In earlier papers of this series, it was proposed that an effect, characterized as *steric enhancement of resonance*, might explain progressive bathochromic displacements of ultraviolet maxima and longer wavelength band edges with increasing bulk of the substituent group in the 1-alkyl-2,4-dinitrobenzenes,[1] 1-alkyl-2,4,6-trinitrobenzenes,[2] and N,N-dialkyl-2,4-dinitroanilines.[3] We wish now to suggest that the same phenomenon accounts for spectral shifts in the N-alkyl- and N,N-dialkylpicramides, and discuss some aspects of conformation which may be deduced from the spectra.

The ultraviolet spectrum of picramide (1) in methanol shows two N→V bands above 250 mμ (Table I and Figure 1). From comparison with 2-nitro-, 4-nitro-, 2,4-dinitro- and 2,6-dinitroaniline spectra,[3] the max-

TABLE I

SPECTRA OF PICRAMIDE DERIVATIVES IN METHANOL[a]

		$(R_2{}^+N{=}C_1{\rightarrow}C_4{=}NO_2{}^-)$ transition			$(R_2{}^+N{=}C_1{\rightarrow}C_2{=}NO_2{}^-)$ transition		
	Picramide	λ_{max}, mμ	ν_{max}, cm^{-1}	ϵ_{max}	λ_{max}, mμ	ν_{max}, cm^{-1}	ϵ_{max}
1.	Unsubstituted	318	31,450	12,000	407	24,570	7,900
2.	N-Methyl-	337	29,670	14,700	408	24,510	6,290
3.	N-Ethyl-	338	29,590	14,960	410	24,390	6,120
4.	N-Isopropyl-	337.5	29,630	14,330	410	24,390	5,610
5.	N,N-Dimethyl-	(335)	(29,850)	(9,400)			
		371	26,950	11,670			
6.	N,N-Diethyl-	(335)	(29,850)	(6,750)			
		384	26,040	10,200			

[a] Values in parentheses are for shoulders or inflections.

(1) H. G. Adolph, B. Johnson, and M. J. Kamlet, *J. Org. Chem.*, **30**, 2864 (1965).

(2) M. J. Kamlet, J. C. Hoffsommer, and H. G. Adolph, *J. Amer. Chem. Soc.*, **84**, 3925 (1962).

(3) M. J. Kamlet, H. G. Adolph, and J. C. Hoffsommer, *ibid.*, **86**, 4018 (1964).

imum at 318 mμ (ε 12,000) has been attributed to the ($H_2{}^+N{=}C_1{\rightarrow}C_4{=}NO_2{}^-$) electronic transition, and that at 407 mμ (ε 7900) has been attributed to the two mutually equivalent ($H_2{}^+N{=}C_1{\rightarrow}C_2{=}NO_2{}^-$) transitions. This band assignment has received confirmation in a novel manner.[4] Spectra of **1** and 2,3,4,6-tetranitroaniline in dioxane were compared and, based on the above assignments, the angles of twist from planarity, θ, of the 4-nitro substituent in the latter compound was estimated from Braude's relationship[5] (eq 1) and

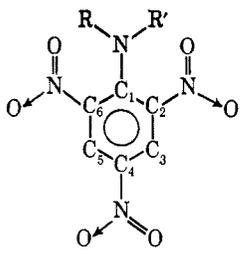
$$\cos^2\theta = \epsilon/\epsilon_0 \quad (1)$$

the angle of twist of the 2-nitro substituent from a modification of the expression in eq 1 (eq 2). These angles

$$\cos^2\theta = (\epsilon - {}^1/_2\epsilon_0)/{}^1/_2\epsilon_0 \quad (2)$$

of twist estimated from the spectra corresponded closely to values of θ observed in a total crystal structure determination.[4,6]

On N-alkylation of **1** [N-methyl- (**2**), N-ethyl- (**3**) and N-isopropylpicramide (**4**)], two effects are observed in the spectra: (a) progressive reductions in intensity of the ($RH^+N{=}C_1{\rightarrow}C_2{=}NO_2{}^-$) band with increasing bulk of R, but with no appreciable displacement in position, and (b) bathochromic–hyperchromic shifts of the ($RH^+N{=}C_1{\rightarrow}C_4{=}NO_2{}^-$) band from 318 to 337–338 mμ.



1, R = R′ = H
2, R = CH_3; R′ = H
3, R = C_2H_5; R′ = H
4, R = $(CH_3)_2CH$; R′ = H
5, R = R′ = CH_3
6, R = R′ = C_2H_5

The first of these effects is readily rationalized in terms of classical steric inhibition of resonance. Maximum resonance stabilization in **2–4** is achieved in the conformer wherein the alkylamino group remains coplanar with the ring. The resulting molecular crowding imposes a twist from planarity on one of the *o*-nitro groups, with consequent diminished absorption intensity in the electronic transition involving this substituent.

It is possible to arrive at some rough estimates of the values of θ for these twisted *o*-nitro groups. The 408–410-mμ bands of **2–4** are superimposed on the tails of the 337–338-mμ bands. Assuming that the latter resemble the spectral envelopes for the corresponding N-alkyl-4-nitroanilines (*i.e.*, the same ratio of ϵ/ϵ_{max} at the same $\Delta\nu$), these tails would in each case contribute

(4) C. Dickinson, J. R. Holden, and M. J. Kamlet, *Proc. Chem. Soc.*, 232 (1964).

(5) E. A. Braude in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, p 172.

(6) C. Dickinson, J. M. Stewart, and J. R. Holden, *Acta Crystallogr.*, **21**, 663 (1966).

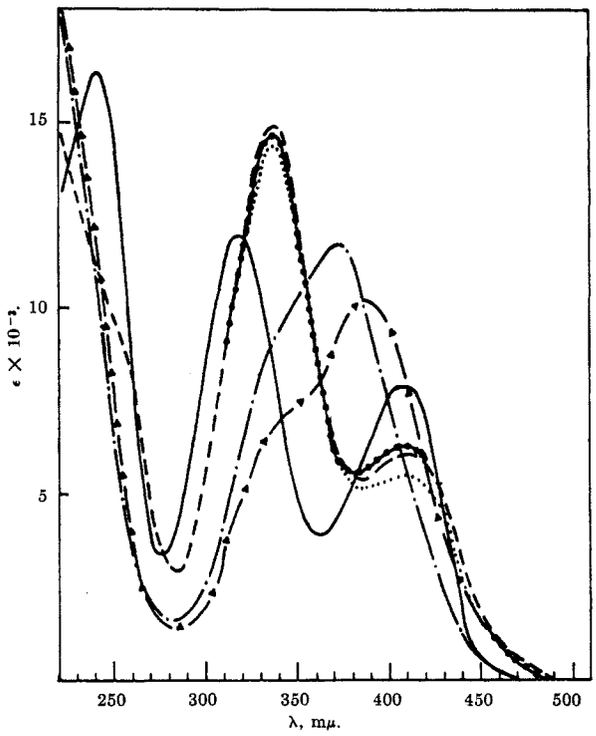


Figure 1.—Spectra of picramide derivatives in methanol: picramide, ———; N-methyl, —•—•—•—; N-ethyl, — — — —; N-isopropyl, ...; N,N-dimethyl, —·—·—; N,N-diethyl, —▲—▲—.

~1700 to ϵ_{409} of **2–4**.[7] The residual molar extinction coefficients due to the ($RH^+N{=}C_1{\rightarrow}C_2{=}NO_2{}^-$) transitions would therefore be ~4590 for **2**, ~4420 for **3**, and ~3910 for **4**. Assuming that the unhindered *o*-nitro groups in **2–4** remain totally coplanar, and that their full contributions to ϵ_{max} of the 408–410-mμ bands are realized, the angles of twist of the displaced nitro groups may be calculated from eq 2.[7] These estimated values of θ are 66° for **2**, 70° for **3**, and 90° for **4**.

The influence of substituents on the 318-mμ band of **1** requires more detailed analysis. N-Alkylation has a bathochromic–hyperchromic effect on the spectra of most aniline derivatives.[3,8] This is attributed to inductive electron release by alkyl which results in increased ground-state electron density on nitrogen and consequently lower energy requirements in the ($RH^+N{=}C_1{\rightarrow}C_4{=}X^-$) electronic transition. Whereas such must account, in part, for the 19–20-mμ spectral displacements in **2–4** relative to **1**, the further effect, *sterec enhancement of resonance*, may also come into play.

As the *o*-nitro groups are twisted from planarity in **2–4**, they exert only fractional electron withdrawal (inductive but not mesomeric). Ground-state electron densities on the amine nitrogens are therefore higher than in hypothetical totally coplanar **2–4** and the ($RH^+N{=}C_1{\rightarrow}C_4{=}NO_2{}^-$) electronic transition energies are lowered further. In effect ($RHN{-}C_1{=}C_4{-}NO_2 \leftrightarrow RH^+N{=}C_1{\rightarrow}C_4{=}NO_2{}^-$) resonance is enhanced in consequence of the steric interactions between N-alkyl and *o*-nitro which inhibit ($RHN{-}C_1{=}C_2{-}NO_2 \leftrightarrow RH^+N{=}C_1{\rightarrow}C_2{=}NO_2{}^-$) resonance.

(7) Band overlap in **1** is appreciably less than in **2–4** (Figure 1). From similar reasoning, the contribution of the tail of the 318-mμ band to absorption at 407 mμ is almost nil. The full value of 7900 is therefore taken for ϵ_0 in the calculations.

(8) M. J. Kamlet, *Israel J. Chem.*, **1**, 428 (1963).

We may evaluate the relative magnitudes of inductive and steric effects by comparing spectral displacements on N-alkylation ($\Delta\nu_{max}$, Table II) in the picramide series with those in the 4-nitro- and 2,4-dinitroanilines,[9] where the inductive but not the steric effect is observed.[10] In the latter two series, the spectral shifts in the N-methyl- and N-ethyl- relative to the unsubstituted derivatives are about the same, $\Delta\nu_{max}$ -1020 to -1050 cm^{-1}.[3] In **2** relative to **1**, however, $\Delta\nu_{max}$ -1780 cm^{-1}, and in **3** relative to **1**, Δ_{max} -1860 cm^{-1}. We attribute these increased displacements ($\Delta\Delta\nu_{max}$ -730 and -810 cm^{-1}) to the *steric enhancement of resonance* phenomenon.

TABLE II

SPECTRAL DISPLACEMENTS ON N-ALKYLATION, ($R_2{}^+N{=}C_1{\rightarrow}C_4{=}NO_2{}^-$) BAND

	$\Delta\nu_{max}(\nu_{max} - \nu_{max}^{X=NH_2})$, cm^{-1}			Contribution of steric enhancement,
X	4-$NO_2C_6H_4X$	2,4-$(NO_2)_2$-C_6H_3X	2,4,6-$(NO_2)_3$-C_6H_2X	$\Delta\Delta\nu_{max}$, cm^{-1}
CH_3NH–	-1050	-1020	-1780	-730
C_2H_5NH–	-1050	-1020	-1860	-810
$(CH_3)_2N$–	-1310	-2590[a]	-4500	-3190
$(C_2H_5)_2N$–	-1540	-3090[a]	-5410	-3870[b]

[a] These shifts also show the effects of steric enhancement of resonance.[3] [b] Includes contribution of ring deformation; see text.

The spectral effects of *steric enhancement of resonance* are more pronounced, albeit with some complications, in N,N-dimethyl- (**5**) and N,N-diethylpicramide (**6**), which show single maxima at 371 mμ (ϵ 11,670) and 384 mμ (ϵ 10,200), respectively. The complications arise from the lowered absorption intensities in **5** and **6** relative to **2** and **3**,[11] and from a minor shoulder at ~335 mμ in **5** which becomes more strongly evident in **6** (Figure 1).

Possible ($R_2{}^+N{=}C_1{\rightarrow}C_2{=}NO_2{}^-$) bands in the dialkylpicramides may be disposed of summarily. Both the 2- and the 6-nitro groups appear to be sufficiently twisted from planarity in all stable conformers that any absorptions at 400–425 mμ due to such *ortho* interactions[12] are of sufficiently low intensities that not even inflections may be discerned on the longer wavelength band edges to mark their contributions to the spectral envelopes of **5** or **6**.

Substituent effects on the ($R_2{}^+N{=}C_1{\rightarrow}C_4{=}NO_2{}^-$) electronic transition may be rationalized on the assumption that **5** and **6** exist, in each case, as mixtures of two comparably stable rotational conformers, A and B: rotomers **5A** and **6A** in which the two *o*-nitro groups are twisted and the dialkylamino groups are essentially coplanar with the rings [possibly the C_1—C_2—$N(O_2)$ and the C_1—C_6—$N(O_2)$ bond angles are expanded from 120° and the C_1—C_2 and C_1—C_6 bond distances are increased from normal values to allow this coplanarity]; rotomers **5B** and **6B** in which the nitro groups are twisted as before, but increasing steric requirements also impose a twist (or possibly a folding back from planarity) on the dialkylamino groups.[13]

From *a priori* considerations, it would be expected that the A rotomers would become decreasingly stable relative to the B rotomers and that the population of the latter would increase with increasing bulk of the alkyl substituents. On this basis the weakening 371- and 384-mμ maxima are attributed to the ($R_2{}^+N{=}C_1{\rightarrow}C_4{=}NO_2{}^-$) electronic transitions in rotomers **5A** and **6A**; the strengthening 335-mμ inflections are attributed to the same electronic transitions, but in rotomers **5B** and **6B**.

It is convenient to examine the phenomena which come into play on N,N-dialkylation of picramide by considering first the effects on the A rotomers of **5** and **6** relative to **1**–**4**, then on the B rotomers, and finally on the summations as reflected in the total spectral envelopes.

In **5A** and **6A** the maxima are displaced by -4500 and -5410 cm^{-1}, respectively, relative to **1** ($\Delta\nu_{max}$, Table II). These compare with shifts of -1310 and -1540 cm^{-1}, respectively, for N,N-dimethyl- and N,N-diethyl-4-nitroaniline relative to 4-nitroaniline, which reflect the inductive influence of two alkyl groups. The increased spectral displacements ($\Delta\Delta\nu_{max}$) we attribute, as before, to *steric enhancement of resonance*. The 2- and 6-nitro substituents exert only fractional electron withdrawal compared with hypothetical totally coplanar **5** and **6**. The electron densities on amine nitrogens are consequently higher, and the ($R_2{}^+N{=}C_1{\rightarrow}C_4{=}NO_2{}^-$) electronic transition energies are consequently lower.

With **5B** and **6B** two offsetting phenomena influence the band positions and intensities. Noncoplanarity of the 2- and 6-nitro groups introduces steric enhancement; noncoplanarity of the dialkylamino group introduces steric inhibition of ($R_2N{-}C_1{=}C_4{-}NO_2 \leftrightarrow R_2{}^+N{=}C_1{\rightarrow}C_4{=}NO_2{}^-$) resonance. The former effect is strongly bathochromic and weakly hyperchromic; the latter is weakly hypsochromic and strongly hypochromic (lowers ϵ). In combination, these phenomena lead to positions of the shoulders in **5** and **6** which do not differ markedly from those of the maxima for the monoalkyl derivatives **2**–**4**. The dominant result is in a strongly reduced absorption intensity (steric inhibition in the B rotomer).

Summations for the mixtures of rotomers, *i.e.*, total spectral envelopes attributable to ($R_2{}^+N{=}C_1{\rightarrow}C_4{=}NO_2{}^-$) transitions, show appreciable band broadening in **5** and **6** relative to **2**–**4** (compare band widths at half-heights) and decreasing integrated absorption intensities as the population of the B rotomer increases.

One further question deserves discussion. If, as the spectrum seems to show, the angles of twist of the 2- and 6-nitro groups already approach 90° in the A rotomer of **5**, why is there an increased $\Delta\Delta\nu_{max}$ in going from **5A** to **6A**? It has been mentioned that, to ac-

(9) No steric effect is observed in the monoalkyl-2,4-dinitroanilines which can easily assume the *s-trans* conformation, but steric enhancement is observed in this series on dialkylation.[3]

(10) A further minor complication due to the effects of changing hydrogen bonding on the spectra is discussed in ref 8, but has been ignored here. If the influence of changing hydrogen bonding is taken into account in all three series, the spectral displacements ascribed to steric enhancement become slightly greater.

(11) The normal effect of N-alkylation is hyperchromic as was observed in **2** and **3** relative to **1**. In the 4-nitroaniline series the order of extinction coefficients is $Et_2N > Me_2N = EtNH > MeNH > H_2N$; in the 2,4-dinitroaniline series the order is $Et_2N = Me_2N > EtNH = MeNH > H_2N$.[3]

(12) Positions of the ($R_2{}^+N{=}C_1{\rightarrow}C_2{=}NO_2{}^-$) bands in 2-nitroanilines are displaced relatively little from 400 to 410 mμ by a wide variety of N and ring substituents.[3]

(13) A contrary viewpoint has been taken by Gould, who suggests that a 4.8 unit increase in pK relative to **1** derives from a preferred conformation in **5** wherein the 2- and 6-nitro groups remain coplanar and the dialkylamino group is twisted from planarity: E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 237. While the latter conformation is inconsistent with the spectra, the conformations suggested here are completely consistent with the pK values.

commodate coplanar dialkylamino groups, the C_1—C_2—$N(O_2)$ and C_1—C_6—$N(O_2)$ angles in A rotomers might be expanded from 120° and C_1—C_2 and C_1—C_6 bond distances could also increase from normal values. Internal ring angles might also change, and even bending or folding of the benzene ring is not out of the question.[14] Increased molecular distortions of these types with increasing substituent bulk in compounds closely related to **5** and **6** may be observed in a comparison of total crystal structures of N-nitro-N-methylpicramide (tetryl)[15] and N-nitro-N-trifluoroethylpicramide.[16]

Ingraham has commented on a slight bathochromic effect of molecular distortion in benzene derivatives.[17] Additional effects of these types, which would be expected to increase from dimethyl to diethyl, might account for the increased $\Delta\Delta\nu_{max}$.

It deserves comment that, had we considered the spectrum of **6** *ab initio*, an analysis such as the above would have been all but impossible. Only by examining trends, first on monoalkylation, then on dialkylation, and by observing the progressive growth of one band and concommitant shrinking of another with increasing alkyl bulk, were we able to arrive at the above assignments.

(14) In the crystal, the ring of 2,3,4,6-tetranitroaniline shows a slight boat shape in the C_1—C_4 axis. Bond distances and internal and external bond angles also differ appreciably from normal values.[6]

(15) H. Cady, *Acta Crystallogr.*, **23**, 601 (1967).

(16) J. R. Holden and C. Dickinson, to be published.

(17) L. L. Ingraham in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p 500.

Experimental Section

All materials were commercially available or prepared by literature methods from picryl chloride and the appropriate mono- or dialkylamine. They were purified by standard means to meet conventional spectrophotometric criteria of purity. Absorption spectra were determined in methanolic solution using a Cary Model 14 recording spectrophotometer with matched 1-cm silica cells. Concentrations were 3–5 × 10^{-5} *M*. Previously described precautions[18] were taken to guard against photochemical transformations.

Registry No.—**1**, 489-98-5; **2**, 1022-07-7; **3**, 7449-27-6; **4**, 16876-54-3; **5**, 2493-31-4; **6**, 13029-07-7.

Acknowledgments.—Helpful discussions with Drs. J. C. Dacons and L. A. Kaplan and Messers. C. Dickinson and D. J. Glover are gratefully acknowledged. The work was done under Foundational Research Task FR-44 of the U. S. Naval Ordnance Laboratory.

(18) M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957).

Fluoronitroaliphatics. II. Fluorodinitromethyl Compounds. Synthetic Approaches and General Properties[1]

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Preparative procedures are described for a new class of compounds containing the $FC(NO_2)_2$– moiety. Three general synthesis methods are most useful in this series: (1) fluorination of 1,1-dinitro carbanion salts with perchloryl fluoride; (2) aqueous fluorination of 1,1-dinitro carbanions (the Grakauskas reaction); (3) reactions of fluorotrinitromethane with a variety of nucleophiles.

In the course of studies concerning the chemistry of polynitroaliphatic compounds, a program was initiated at this laboratory with the aim of developing synthesis methods for fluorodinitromethyl analogs, then undescribed, of known trinitromethyl and other halodinitromethyl compounds.[2–5] In this and the following papers, we wish to report some of the results of this work and, in addition, describe a number of novel fluorodinitromethyl derivatives for which the corresponding $C(NO_2)_3$– or $RC(NO_2)_2$– analogs are as yet unknown.

Pathways for the synthesis of fluorodinitromethyl compounds considered at the outset and during the course of this investigation included (a) introduction of a second nitro group into compounds already containing the fluoronitromethyl function; (b) introduction of two nitro groups into simple or activated monofluorohydrocarbons; (c) introduction of fluorine into 1,1-dinitro compounds. Since 1,1-dinitroalkanes had previously been reported in considerable number and were fairly readily available,[2] we have directed our attention primarily to pathway c.

An analogy for the introduction of fluorine existed in the ease with which 1,1-dinitro carbanions reacted with chlorinating and brominating agents to form the corresponding chloro- and bromodinitromethyl compounds.[2]

$$RC(NO_2)_2^- + Cl_2 \longrightarrow RC(NO_2)_2Cl + Cl^-$$

Accordingly, the problem was one of finding suitable fluorinating agents which would selectively attack the dinitromethyl anion in a manner similar to the reaction with chlorine, while leaving intact as wide as

(1) Part I: H. G. Adolph and M. J. Kamlet, *J. Amer. Chem. Soc.*, **88**, 4761 (1966). See also 1-fluoro-1,1-dinitroalkanes [M. J. Kamlet, U. S. Patent 3,366,697 (Jan 30, 1968)] and 4-fluoro-4,4-dinitrobutyric acid [M. J. Kamlet, U. S. Patent 3,356,714 (Dec. 5, 1967)].

(2) P. Noble, F. G. Borgardt, and W. L. Reed [*Chem. Rev.*, **61**, 19 (1964)] provide a comprehensive review of the polynitroaliphatic chemistry field through 1963.

(3) Occasional reports on fluorodinitromethyl compounds have appeared in the literature during the past year, but these generally make reference to earlier work by us or Grakauskas and Baum (see following paper[4]) in the form of private communications. These include fluorodinitroalkyl esters of monocarboxylic acids [O. S. Schaeffler, U. S. Patent 3,316,292 (April 25, 1967)], fluorodinitroalkane preparation [M. Graff, W. E. McQuistion, and J. W. Sterling, U. S. Patent 3,274,264 (Sept 20, 1966)], and heat of formation and properties of fluorotrinitromethane [M. F. Zimmer, R. A. Robb, E. E. Baroody, and G. A. Carpenter, *J. Chem. Eng. Data*, **11**, 577 (1966)]. While the present paper was in process of revision, a report appeared describing solid phase fluorinations of potassium nitroform and dipotassium 1,1,2,2-tetranitroethane to yield, *inter alia*, some of the products reported here. A fluorine–nitrogen mixture was passed over these salts in a matrix of potassium fluoride and granulated copper.[5]

(4) V. Grakauskas and K. Baum, *J. Org. Chem.*, **33**, 3080 (1968).

(5) L. T. Eremenko, F. Ya. Natsibullin, and I. P. Borovinskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 429, 431 (1968).