[CONTRIBUTION FROM THE ORGANIC CHEMISTRY DIVISION U. S. NAVAL ORDNANCE LABORATORY]

Ultraviolet Absorption Spectra of 1,1-Dinitroalkane Salts

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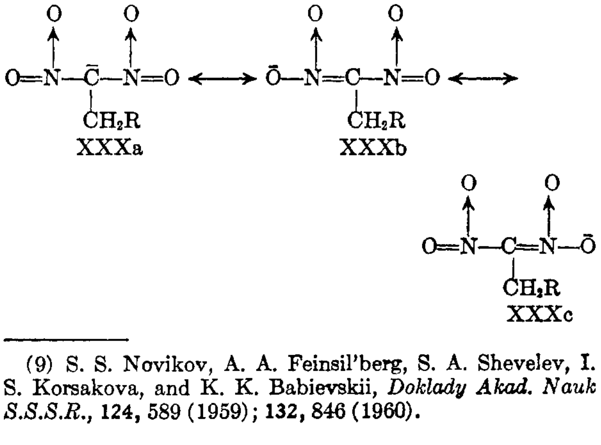
The ultraviolet absorption spectra are described and some correlations with structure drawn for a number of compounds of the type $RC(NO_2)_2^-K^+$. Electronic and steric effects of substituents are discussed and a $\lambda_{max} - \sigma^*$ relationship demonstrated where steric effects are constant.

During recent investigations in polynitroaliphatic chemistry[1-4] we have had frequent occasion to employ their characteristic ultraviolet spectra in the identification and elucidation of structure of 1,1-dinitroalkane salts (1-nitroalkane-1-nitronates). Since only a few such spectra are described elsewhere[5,6] we wish now to assemble and record the available data with some observations regarding spectra-structure correlations in this series.

For all compounds in Table I maxima lie in the 310- to 410-mμ region and minima in the 260- to 310-mμ region with ϵ_{min} typically less than 10% of ϵ_{max}, so that positions of λ_{max} are little influenced by complications due to overlap with shorter wave length bands. Since all compounds except XVI–XIX show spectral envelopes which are relatively symmetrical about sharp maxima it is likely that they are individual rather than fused bands and derive from single electronic transitions.[7]

These compounds fall into five general categories: (*a*) Saturated 1,1-dinitroalkane salts, unsubstituted or substituted in the 3-position, show maximal absorption at 379 ± 5 mμ (ϵ = 17,000 ± 1000). This group includes II–V, X–XV and XXIX. (*b*) Compounds VI–VIII and sodium 1,1-dinitro-2-piperidinoethane (XXIV in alkali[8]) comprise a group with electron-withdrawing substituents in the 2-position for which λ_{max} lies at 366 ± 3.5 mμ. (*c*) For the zwitterionic compound 2-amino-1,1-dinitroethane (XXI) and its *N*-substituted derivatives XXII–XXIV, λ_{max} is shifted hypsochromically to 357 ± 5 mμ. (*d*) The 3-substituted 1,1-dinitro-2-propene salts XVI–XIX show two maxima, a relatively sharp peak at 313–326 mμ (ϵ = 16,000–20,000) and a diffuse band at 395–410 mμ (ϵ = 8400–10,000). For the related potassium 1,1,3-trinitro-2-propene (XX) the shorter wave length band is absent and the longer wave length band more than doubled in intensity. (*e*) The dipotassium salts XXV–XXVII absorb in the same range as category *b* with about three-fourths the intensity per nitronitronate group. As might be expected the intensity increases with distance between the absorbing centers.

Spectral distinctions between the various categories have been sufficiently well substantiated by the variety of 1,1-dinitroalkane salts studied to afford strong preliminary indications of the structure of new compounds. For example, the reaction of potassium trinitromethide with acrylamide in absolute methanol yielded two insoluble salt-like products, one yellow, one orange. Based on its characteristic two maxima the orange salt was tentatively identified as an unsaturated compound and further investigation confirmed its structure as potassium 4,4-dinitro-2-butenamide (XVIII).[2] From the single band at 380 mμ (log ϵ = 4.22) typical to category *a*, it was inferred that the yellow product was a saturated dinitroalkane salt *not substituted alpha to the dinitromethyl group.* It was eventually identified as potassium 4,4-dinitro-2-hydroxybutyramide (XV).[2] Spectral evidence also contributed strongly to the identification as potassium 1,1,3-trinitro-2-propene (XX)



$$O{=}\overset{\overset{O}{\uparrow}}{N}-\underset{CH_2R}{\bar{C}}-\overset{\overset{O}{\uparrow}}{N}{=}O \longleftrightarrow \bar{O}-\overset{\overset{O}{\uparrow}}{N}{=}\underset{CH_2R}{C}-\overset{\overset{O}{\uparrow}}{N}{=}O \longleftrightarrow O{=}\overset{\overset{O}{\uparrow}}{N}-\underset{CH_2R}{C}{=}\overset{\overset{O}{\uparrow}}{N}-\bar{O}$$

XXXa XXXb XXXc

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[1] M. J. Kamlet, J. C. Dacons, and J. C. Hoffsommer, *J. Org. Chem.*, **26**, 4881 (1961).

[2] L. A. Kaplan and M. J. Kamlet, *Abstracts Papers Amer. Chem. Soc.*, **137**, 56–O (1960).

[3] M. J. Kamlet and J. C. Dacons, *J. Org. Chem.*, **26**, 3005 (1961).

[4] D. J. Glover and M. J. Kamlet, *J. Org. Chem.*, **26**, 4734 (1961).

[5] G. Kortum, *Z. physik. Chem.*, **B43**, 271 (1939); *Z. Elektrochem.*, **47**, 55 (1941).

[6] L. Zeldin and H. Shechter, *J. Am. Chem. Soc.*, **79**, 4708 (1957).

[7] For example, II shows a band-width at half-height of 49 mμ with the band-center at half-height at 380 mμ. XXVIII shows a band-width at half-height of 45 mμ with the band-center at half-height at 349 mμ.

[8] The spectrum of XXIV in alkali is undoubtedly that of the 2-piperidino-1,1-dinitroethane anion. For comparison, the spectrum of XXII in alkali is identical with that of VII while the spectrum of VII in neutral media closely resembles that of XXII.

[9] S. S. Novikov, A. A. Feinsil'berg, S. A. Shevelev, I. S. Korsakova, and K. K. Babievskii, *Doklady Akad. Nauk S.S.S.R.*, **124**, 589 (1959); **132**, 846 (1960).

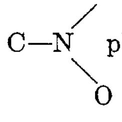
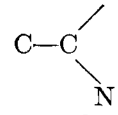
TABLE I

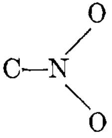
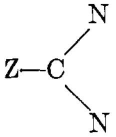
ULTRAVIOLET SPECTRA OF 1,1-DINITROALKANE ANIONS

Compound	Solvent	λ_{max} (log ϵ)
$K^+\ {}^-C(NO_2)_2H$ (I)	dil. KOH	362.5 (4.30)[a]
$K^+\ {}^-C(NO_2)_2CH_3$ (II)	dil. KOH	381.5 (4.23)[a,g]
$K^+\ {}^-C(NO_2)_2CH_2CH_3$ (III)	dil. KOH	382 (4.23)[a]
	alk. CH_3OH	377 (4.29)[a]
	alk. $(CH_3)_2CO$	376 (4.31)[a]
$K^+\ {}^-C(NO_2)_2CH_2CH_2CH_3$ (IV)	dil. KOH	382 (4.20)[a]
$K^+\ {}^-C(NO_2)_2CH_2CH_2CH_2CH_3$ (V)	dil. KOH	382 (4.21)[a]
$K^+\ {}^-C(NO_2)_2CH_2CN$ (VI)	dil. KOH	362.5 (4.28)[a]
$K^+\ {}^-C(NO_2)_2CH_2N(CH_3)_2$ (VII)	dil. KOH	369.5 (4.20)[b]
$K^+\ {}^-C(NO_2)_2CH_2OH$ (VIII)	dil. KOH	365 (4.29)[a]
$K^+\ {}^-C(NO_2)_2C_6H_5$ (IX)	dil. KOH	373 (4.18)[a]
$K^+\ {}^-C(NO_2)_2CH_2CH_2COOCH_3$ (X)	dil. KOH	379 (4.23)[a]
$K^+\ {}^-C(NO_2)_2CH_2CH_2COCH_3$ (XI)	dil. KOH	379 (4.22)[a]
$K^+\ {}^-C(NO_2)_2CH_2CH_2COO^-\ K^+$ (XII)	dil. KOH	382 (4.21)[a]
$K^+\ {}^-C(NO_2)_2CH_2CH_2CONH_2$ (XIII)	dil. KOH	379 (4.21)[a]
$K^+\ {}^-C(NO_2)_2CH_2CH_2COC_6H_5$ (XIV)	dil. KOH	379 (4.21)[a]
$K^+\ {}^-C(NO_2)_2CH_2CHOHCONH_2$ (XV)	dil. KOH	380 (4.22)[e]
$K^+\ {}^-C(NO_2)_2CH{=}CHCN$ (XVI)	H_2O	320 (4.29), 399 (4.00)[e]
$K^+\ {}^-C(NO_2)_2CH{=}CHCOOCH_3$ (XVII)	H_2O	326 (4.24), 399 (3.98)[e]
$K^+\ {}^-C(NO_2)_2CH{=}CHCONH_2$ (XVIII)	H_2O	322 (4.23), 403 (3.97)[e]
$K^+\ {}^-C(NO_2)_2CH{=}CHCOO^-\ K^+$ (XIX)	H_2O	313 (4.20), 410 (3.92)[e]
$K^+\ {}^-C(NO_2)_2CH{=}CHNO_2$ (XX)	H_2O	395 (4.33)[f]
${}^-C(NO_2)_2CH_2\overset{+}{N}H_3$ (XXI)	H_2O	362 (4.19)[b]
${}^-C(NO_2)_2CH_2\overset{+}{N}H(CH_3)_2$ (XXII)	H_2O	357 (4.25)[b]
${}^-C(NO_2)_2CH_2\overset{+}{N}(CH_3)_3$ (XXIII)	dil. NaOH	352 (4.17)[d]
${}^-C(NO_2)_2CH_2\overset{+}{N}HC_5H_{10}$ (XXIV)	H_2O	357 (4.15)[d]
	dil. NaOH	369 (4.05)[d]
$K^+\ {}^-C(NO_2)_2CH_2C(NO_2)_2{}^-K^+$ (XXV)	dil. KOH	367 (4.41)[b,c]
$K^+\ {}^-C(NO_2)_2C(NO_2)_2{}^-\ K^+$ (XXVI)	dil. KOH	362.5 (4.41)[a]
$K^+\ {}^-C(NO_2)_2CH_2NHCH_2C(NO_2)_2{}^-\ K^+$ (XXVII)	dil. KOH	367 (4.46)[b,c]
$K^+\ {}^-C(NO_2)_3$ (XXVIII)	H_2O	350 (4.16)[a]
$K^+\ {}^-C(NO_2)_2CH_2CH_2NO_2$ (XXIX)	H_2O	373.5 (4.24)[f,h]

[a] Spectra determined in present investigation. [b] Ref. 3. [c] Photosensitive; fades on exposure to actinic radiation. [d] Ref. 6. [e] Ref. 2. [f] Ref. 1. [g] Zeldin and Shechter[6] report 381 (4.21). [h] Fades in dilute alkali.

of a compound which had been reported as potassium 1,1,3-trinitropropane (XXIX).[1,9]

The following resonance structures might be expected to contribute to both ground and electronic excited states of the 1,1-dinitroalkane anions. On steric and electronic grounds it might be assumed that the most stable conformation would involve an N—C—N angle greater than 120° with corresponding contraction of the C—C—N angles. Oxygen-oxygen repulsions would probably also cause skewing of the individual  planes from the  plane so that resonance interaction between the individual nitro groups is not at a maximum.

It follows that the greater the bulk of Z in Z—C-$(NO_2)_2^-$ the more difficult it is to contract the Z—C—N angles, the less the N—C—N angle, the greater the effect of O—O repulsions, the greater the angle of skew of the  planes from the  plane, and the less the resonance interaction between the nitro groups. Novikov and coworkers[10] have pointed out that 1,1-dinitro-2-methylpropane is a twenty-fold weaker acid then a series of unbranched 1,1-dinitroalkanes. An increased angle of skew with lessened resonance interaction between the nitro groups in the conjugate anion of this compound relative to the conjugate anions of the unbranched dinitroalkanes may have contributed to this effect. Conversely,

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(10) S. S. Novikov, V. M. Belikov, A. A. Feinsil'berg, L. V. Ershova, V. I. Slovetskii, and S. A. Shevelev, *Izv. Akad. Nauk S.S.S.R., Otdel Khim. Nauk*, 1855 (1959).

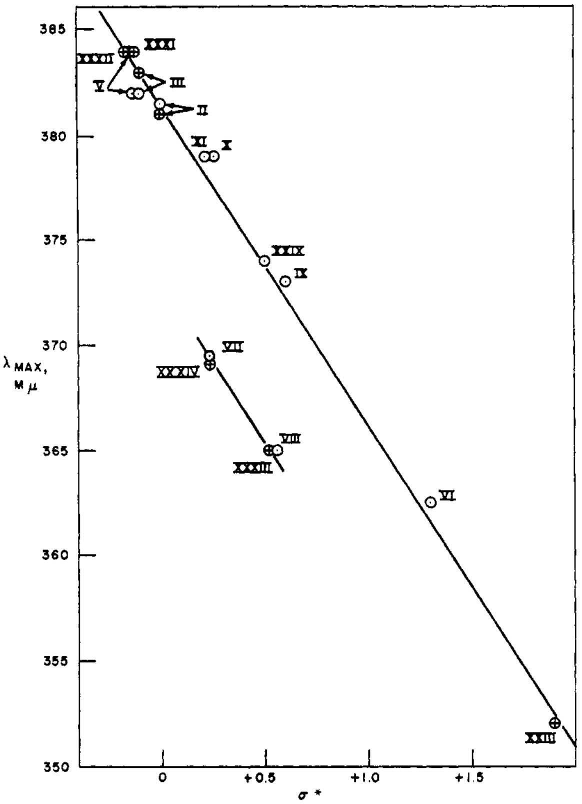


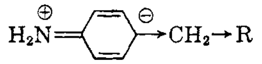
Fig. 1. λ_{max} related to σ*. ⊙-Present investigation. ⊕-Data of Shechter.[23]

the enhanced acidity of dinitromethane[11] relative to other 1,1-dinitroalkanes[10,12] may in part be due to a greater N—C—N angle in the energetically preferred conformation of the conjugate anion with a lesser angle of skew and increased resonance interaction between the nitro groups.

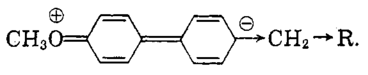
In attempting to assess the *electronic* effects of substituents on the spectra of $Z—C(NO_2)_2^-$ we will therefore attempt to minimize the effects of such *steric* factors[13] by confining ourselves (with one exception) to the situation in which $Z = RCH_2$. The assumption that substituents beta to the dinitromethide function exert only slight steric effects appears to be justified on the basis that 1,1-dinitro-3-methylbutane shows about the same acid strength as the unbranched nitroparaffins.[10]

Some interesting observations may be made in comparing the series $RCH_2C(NO_2)_2^-$, where the order of increasing inductive electron withdrawal by the substituent is R = CH_3 (III) < H (II) < CH_3COCH_2 (XI) < HO (VIII) < $(CH_3)_2N$ (VII) < CN (VI) < $(CH_3)_3\overset{+}{N}{}^+$ (XXIII). In this series increased displacement of the C—C electron pair in the direction of R with progressive lessening of electron density at the dinitromethide function (which should tend to stabilize all resonance structures) is paralleled by hypsochromic displacement of λ_{max}.

This is contrary to experience with p → π* or π → π* transitions of unchanged molecules (B-bands[14]) in which it has been the general rule that inductive or inductomeric delocalization of charge in dipolar resonance structures leads to bathochromic displacement of λ_{max}). For example, Burawoy and Spinner[15] have reported that B-band maxima in the series *p*-$NH_2C_6H_4CH_2R$ and *p*-$CH_3OC_6H_4C_6H_4CH_2R$ are shifted to longer wavelengths with increasing electron-withdrawing ability of R. They have attributed this shift to stabilization of the canonical resonance structures



and



For the series $NO_2C_6H_4CH_2R$, where the CH_2R group was adjacent to a positive charge in the more stable dipolar resonance structures, the effect was as anticipated in the opposite direction.

It is, of course, implicit in spectra-structure correlations that dipolar resonance structures contribute more strongly to electronic excited states in p → π* and π → π* transitions of uncharged molecules than to ground states, so that factors which stabilize these dipolar resonance structures lead to decreased transition energies. This generalization apparently cannot be extended to the spectra of charged molecules of the present type[16] for which less distinction can be drawn between ground and electronic excited states on the basis of classical resonance structures and for which the accepted rationale is that the "distribution of the 'resonating' charge between the several available positions becomes momentarily altered under the influence of the light field."[17]

From quantum mechanical considerations Dewar has suggested that electron-attracting substituents at "unstarred" positions (*i.e.*, unavailable as a "seat for the resonating charge") should shift charge-resonance spectra of anions hypsochromically.[18] The results for the $RCH_2C(NO_2)_2^-$ series conform with this expectation. To explain the more de-

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(11) A. Hantzsch and A. Veit, *Ber.*, **32**, 607 (1899).

(12) J. S. Belew and L. G. Hepler, *J. Am. Chem. Soc.*, **78**, 4005 (1956).

(13) Dr. Harold Shechter, Ohio State University, has appraised us of work in his laboratories relating the effects of substituents in the 2- position to acidities of $R_1R_2R_3CC(NO_2)_2H$ and spectra of $R_1R_2R_3CC(NO_2)_2^-$. Further discussion of this aspect of the problem will be left to Dr. Shechter.

(14) In the band-nomenclature system of W. F. Forbes, *Can. J. Chem.*, **36**, 2350 (1958), the B-band corresponds to the first primary band of Doub and Vandenbelt, the C-band of Klevins and Platt and the K-band of the British school.

(15) A. Burawoy and E. Spinner, *J. Chem. Soc.*, 2557 (1955).

(16) See the last paragraph of the discussion.

(17) E. A. Braude in E. A. Braude, and F. C. Nachod, *The Determination of Organic Structures by Physical Methods*, Academic, New York, 1955, p. 157.

(18) M. J. S. Dewar, *J. Chem. Soc.*, 2329 (1950).

tailed effects of R, however, it may be profitable in the present case to adopt a perhaps more naive viewpoint and examine individual resonance structures.[19]

If, as is not unreasonable, the electronic excited state partakes more of the canonical structures XXXb–c and the ground state more of XXXa, stabilization of XXXb-c relative to XXXa should lead to decreased transition energies and higher λ_{max}. Factors which stabilize XXXa relative to XXXb-c, on the other hand, should cause increased transition energies, lower λ_{max}. While charge dispersal by withdrawal of the C—C electrons in the direction of R should stabilize all resonance structures, it is likely that the effect would be greatest on structure XXXa where the formal charge is adjacent to the C—C bond. This is an example of the latter type of behavior and would account for the hypsochromic displacements.

Although attempts at rho-sigma correlation in ultraviolet spectroscopy have on the whole proven unsuccessful[20] it was considered that in this special case where purely inductomeric effects were involved a quantitative relationship might apply. Taft's σ^*, the best available index of the ability of substituents to withdraw electrons inductomerically[21] was the parameter chosen for comparison.[22] Data for compounds of Table I for which σ^* of the substituent was known or could be estimated by applying a factor of 2.8 to a homolog are listed in Table II and plotted as circles in Figure 1. Also listed in Table II and plotted as crosses in Figure 1 are Shechter's data for salts of 3-methyl-1,1-dinitrobutane (XXXI), 3,3-dimethyl-1,1-dinitrobutane (XXXII) and 2-ethoxy-1,1-dinitroethane (XXXIII).[23]

TABLE II. λ_{max} RELATED TO σ^*

No.	R—C(NO$_2$)$_2^-$, R =	σ^*	λ_{max}, mμ
XXXII	t-$C_4H_9CH_2$	−0.165	384[a]
XXXI	i-C_4H_9	−0.130	384[a]
V	n-C_4H_9	−0.125	382 (384)[a]
III	C_2H_5	−0.100	382 (383)[a]
II	CH_3	0.000	381.5 (381)[c]
XI	$CH_3COCH_2CH_2$	+0.214[d]	379
VII	$(CH_3)_2NCH_2$	+0.22[e]	369.5
XXXIV	$C_5H_{10}NCH_2$[b]	+0.22[h]	369[c]
X	$CH_3OOCCH_2CH_2$	+0.255[f]	379
XXIX	$NO_2CH_2CH_2$	+0.50	374
XXXIII	$CH_3CH_2OCH_2$	+0.52[g]	365[a]
VIII	$HOCH_2$	+0.555	365
IX	C_6H_5	+0.600	373
VI	$N{\equiv}CCH_2$	+1.300	362.5
XXIII	$(CH_3)_3\overset{+}{N}CH_2$	+1.90	352[c]

[a] Ref. 23. [b] Ref. 8. [c] Ref. 6. [d] Estimated by dividing value for CH_3COCH_2 by 2.8. [e] R. W. Taft and I. C. Lewis, *J. Am. Chem. Soc.*, 80, 2436 (1958). [f] Estimated by dividing value for C_2H_5OOC by (2.8).[8] [g] Estimated to be same as value for CH_3OCH_2. [h] Estimated to be same as value for $(CH_3)_2NCH_2$.

Of the fifteen dinitroalkane anions, the λ_{max} *vs.* σ^* plot shows eleven clustering about a straight line. Using our values for II, III and V, the linear relationship is described by the equation,

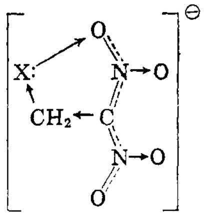
$$\lambda_{max} = (381.6 - 15.25\,\sigma^* \pm 0.7)\ \text{m}\mu$$

Using Shechter's values for II, III, and V the scatter is even less. Compounds VII, VIII, XXXIII and sodium 1,1-dinitro-2-piperidinoethane (XXXIV),[8] the deviants, all show λ_{max} 8–9 mμ lower than the relationship would predict and have in common a pair of non-bonded electrons on the atom beta to the dinitromethide function. If the expression is modified as follows,

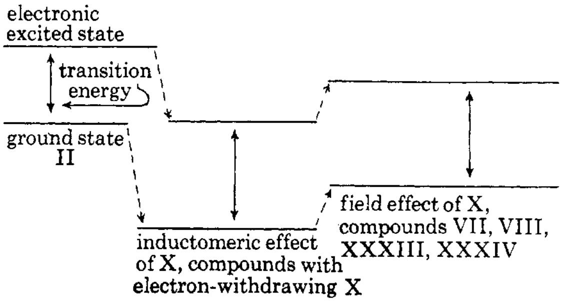
$$\lambda_{max} = (381.6 - 15.25\,\sigma^* - 8.5\,\gamma)\text{m}\mu$$

where γ is 1.0 or 0.0 depending on the presence or absence of non-bonded electrons on the beta atom, all fifteen points fit, the average deviation being less than 0.5 mμ.

An attractive explanation for the additional 8–9 mμ hypsochromic displacement in the case of the latter four compounds would take into account the field effect of the non-bonded electrons. Such a field effect would be expected to destabilize all resonance structures and, from geometrical considerations, would be greater on the canonical structures XXXb–c than on XXXa. Electronic excited state energy should consequently be



further raised relative to ground state energy with a corresponding additional increase in transition energy as represented below.



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(19) We may simply be restating Dewar's concept in terminology more familiar to the physical-organic chemist.

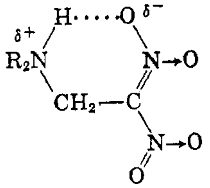
(20) L. Freedman and G. O. Doak, *J. Org. Chem.*, 21, 811 (1956).

(21) R. W. Taft, Jr., in M. S. Newman, *Steric Effects in Organic Chemistry*, Wiley, New York, 1956, chapter 13.

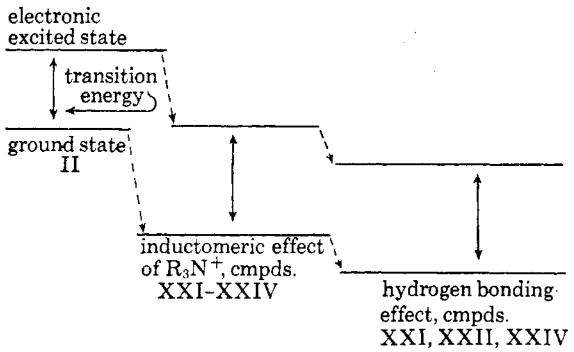
(22) This portion of the discussion has appeared in part in a preliminary communication; M. J. Kamlet and D. J. Glover, *Tetrahedron Letters*, No. 27, 17 (1960).

(23) We are grateful to Dr. H. Shechter for making available to us this unpublished information. In Dr. Shechter's laboratories II was found to have λ_{max} at 381 mμ, III at 383 mμ and IV at 384 mμ. These data are also plotted as crosses in Fig. 1 together with our own data for these compounds.

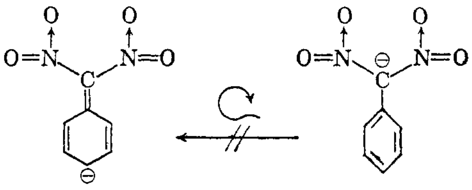
If inductomeric and field effects were the only factors influencing their spectra, one would expect λ_{max} for the zwitterionic compounds to decrease in the order: 2-trimethylammonium-1-nitroethyl-1-nitronate (XXIII) > 2-dimethylammonium-1-nitroethyl-1-nitronate (XXII) ≅ 2-piperidinium-1-nitroethyl-1-nitronate (XXIV) > 2-ammonium-1-nitroethyl-1-nitronate (XXI). The observed order was the converse, XXI > XXIV = XXII > XXIII. Kamlet and Dacons have commented that of these four compounds only XXIII was moderately soluble in water, the rest quite insoluble.[3] This, together with the failure of XXI to undergo many typical reactions of 1,1-dinitroalkane anions, led them to suggest hydrogen bonding.



Such hydrogen bonding would result in charge-delocalization but, referring back to the earlier discussion, the primary effect would be on structures XXXb-c rather than XXXa. This would lower excited state energy relative to ground state and have a bathochromic effect on spectra. By considering the opposing effects, the relative positions of the maxima of the zwitterionic compounds are now readily explained. All are displaced hypsochromically relative to potassium 1,1-dinitroethane because of strong inductomeric electron-withdrawal by the $\overset{+}{R_3N}$ group but the maxima of XXI, XXII and XXIV fall at longer wavelengths than that of XXIII because all but the latter are capable of internal hydrogen bonding. A schematic representation is as follows.

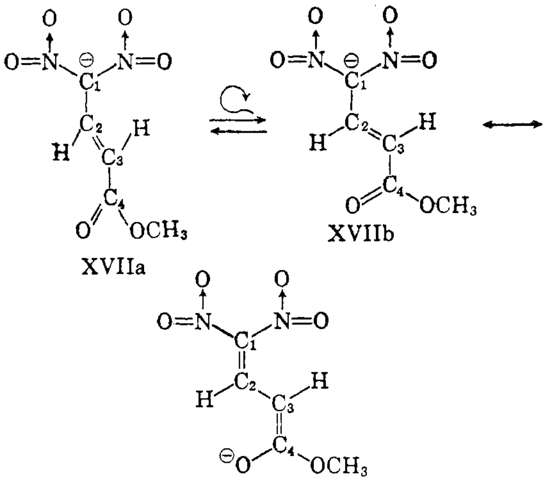


It is significant that the spectrum of potassium phenyldinitromethane (IX) fits the λ_{max} vs. σ^* relationship to within one-half millimicron. This provides excellent evidence that the phenyl group exerts a purely inductomeric effect and that there is no contribution due to resonance structures like IXa. It follows that in the preferred conformation the angle between the plane of the ring and the N—C—N plane approaches 90° (IXb) as would be anticipated from purely steric considerations.



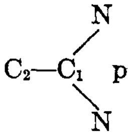
IXa IXb

The spectra of the 1,1-dinitro-2-propene derivatives XVI–XIX are less readily susceptible to detailed interpretation because of the considerable overlap between the two bands which strongly affects the positions of λ_{max}. To relate the spectrum of potassium methyl 4,4-dinitro-2-butenoate (XVII), a representative of the group, to the saturated dinitroalkane anions, several rotomeric conformations of the molecule must be considered.



XVIIa XVIIb XVIIc

In the rotomer XVIIa the C_1-C_2-C_3-C_4-O plane is at an angle of 90° from the N-C_1-N plane. Steric interference between the nitro oxygen and the C-3 hydrogen is at a minimum as is resonance interaction of the charge center with the conjugated system. The carbomethoxyvinyl group exerts a purely inductomeric effect and one would anticipate a hypsochromic shift of λ_{max} relative to II such as was observed with potassium phenyldinitromethane for similar reasons.

In the rotomer XVIIb-c, the nitro nitrogens are coplanar with C-1,C-2, C-3, C-4 and O, and steric interference is increased (possibly causing increased skewing of the nitro oxygens from the  plane). Resonance interaction between the dinitromethide function and the carbomethoxyvinyl group comes into play and XVIIc becomes an important contributor to both ground and electronic excited states. For this conformation one would anticipate a bathochromic displacement relative to II.[24]

Thus, depending on which rotomer were the more stable, one could rationalize either a red or a blue shift relative to the saturated dinitroalkane anions. The existance of two bands, one displaced bathochromically and one hypsochromically, may indicate that for XVI–XIX the rotomers are of comparable stability and that both exist in solution, each absorbing light as if it were a separate molecular species.

With potassium 1,1,3-trinitro-2-propene (XX) only a single high-intensity band was observed with $\lambda_{max} = 395$ mμ. According to the above argument, this would mean that XX exists in solution primarily in the form of the single rotomer corresponding to XVIIb-c. Enhanced stability of this conformation relative to the non-coplanar conformation would not be unexpected in view of the greater ability of the nitro group to bear the negative charge in the resonance structure corresponding to XVIIc.

If the single maximum for XX arose from a single rotomer and the pairs of maxima in XVI–XIX from pairs of rotomers, the integrated intensity of the single band in the former instance should be comparable to sums of integrated intensities for both bands in the latter instances. Relevent data for compounds XVI, XVIII and XX are listed in Table III and show that this is indeed the case.[25]

TABLE III

$K^+\bar{C}(NO_2)_2CH{=}CH{-}Y$, Y =	Band, λ_{max}, mμ	Integrated Intensity, (l. cm.$^{-1}$/ mole cm.) $\times 10^{-8}$	Relative Integrated Intensity
CN (XVI)	320	0.907	0.65
	398	0.443	0.32
	Total	1.350	Total 0.97
$CONH_2$ (XVIII)	322	0.930	0.67
	403	0.416	0.30
		1.346	0.97
NO_2 (XX)	395	1.391	1.00

A weakness in the above argument is that λ_{max} at 313–326 mμ would lead one to assign σ^* values of +4 to +5 to the non-coplanar CH=CHCOR substituent. Hine and Bailey[26] have reported σ^* values of 1.01–1.08 for such substituents.[27]

We cannot unequivocally assign these particular bands to particular transitions. While intensities and integrated intensities are of the order generally associated with B-band transitions, nonconjugating substituents shift maxima in opposite directions. Solvent effects, however, are similar. As is the general rule with B-band absorption, the maximum of potassium 1,1-dinitropropane was shifted to the red on going from solvents of lower to solvents of higher dielectric constant. It is perhaps also noteworthy that incorporating a vinyl group in the chromophore (compare XX and XXVIII) shifted the maximum 45 mμ to the red. This compares with a 40-mμ shift in going from benzene to styrene, a 36–54-mμ shift in going from substituted nitrobenzenes to correspondingly substituted nitrostyrenes.[28]

EXPERIMENTAL

Materials. Potassium 1,1-dinitroethane (II), propane (III), butane (IV), and pentane (V) were prepared from the 1-chloro-1-nitroalkanes by the ter Meer reaction.[29] Also prepared by literature methods were the potassium salts of dinitromethane (I),[30] 2,2-dinitroethanol (VIII),[30] 3,3-dinitropropionitrile (VI),[31] phenyldinitromethane (IX)[32] and nitroform (XXVIII)[33] and the dipotassium salt of 1,1,2,2-tetranitroethane (XXVI).[34] The remaining compounds were prepared by procedures described in earlier papers from these laboratories.[1–4]

Ultraviolet absorption spectra. Spectra over the range 250–500 mμ were determined on a Cary Model 14 recording spectrophotometer or on a Beckman Model DU. Solutions were 3–5 $\times 10^{-5}$ molar and 1-cm. silica cells were used. Previously described precautions were taken in measuring all spectra[35] and it was found that several of the compounds, particularly XXV and XXVII were photosensitive in dilute solutions.

Integrated intensities were determined by plotting molar absorbancy index as a function of wave number on millimeter graph paper, cutting out the spectral envelope and weighing on a Mettler balance. In each instance the graph was cut vertically at the shorter wavelength minimum, no attempt being made to compensate for the negligible overlap with shorter wave length bands.

Acknowledgment. We are indebted to Dr. R. W. Taft for reviewing an earlier version of this paper and to Dr. H. Shechter, for making unpublished

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(24) In Dewar's model[18] this structure would involve incorporation of an electron-withdrawing group at a "starred" position. A bathochromic shift would be predicted.

(25) We wish to thank the referee who suggested integrated intensities as an excellent test of the concept.

(26) J. Hine and W. C. Bailey, *J. Am. Chem. Soc.*, **81**, 2075 (1959).

(27) It should be noted, however, that the values determined by Hine and Bailey are based on an average for all conformations, coplaner and noncoplanar. It is also possible that pi-electrons in the beta-gamma double bond are similar to nonbonding *p*-electrons in a field effect destabilizing resonance structures XXXb–c relative to XXXa. In addition, the angle of skew of the nitro groups may differ in these cases as compared with the saturated dinitroalkane anions.

(28) M. J. Kamlet and D. J. Glover, *J. Am. Chem. Soc.*, **77**, 5696 (1955).

(29) E. ter Meer, *Ann.*, **181**, 1 (1876).

(30) H. Feuer, G. B. Bachman, and J. P. Kispersky, *J. Am. Chem. Soc.*, **73**, 1360 (1951).

(31) J. Meisenheimer and M. Schwarz, *Ber.*, **39**, 2543 (1906).

(32) G. Ponzio and C. Charrier, *Gazz. Chim. Ital.*, **38I**, 648 (1908).

(33) N. S. Marans and R. P. Zelinski, *J. Am. Chem. Soc.*, **72**, 5329 (1950).

(34) R. Scholl and M. Brenneisen, *Ber.*, **31**, 642 (1898).

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

information available to us, and for valuable suggestions. We wish also to thank Dr. Horst Adolph for determining the integrated intensities and to acknowledge helpful discussions with Drs. D. V. Sickman, J. C. Dacons, and L. A. Kaplan.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN]

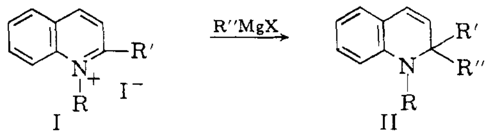
Dihydroquinolines. I. The Action of Metal Hydrides on Quaternary Quinolinium Salts[1]

ROBERT C. ELDERFIELD AND BRUCE H. WARK[2]

Received September 1, 1961

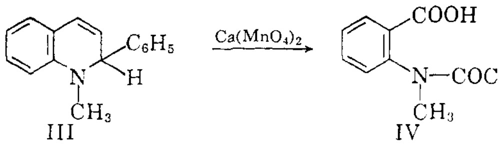
Reduction of a series of quinolinium salts with lithium aluminum hydride and sodium borohydride results in the formation of mixtures of dihydro- and tetrahydroquinolines. The relative proportions of the products formed is affected by the solvent, the temperature at which the reduction is performed and by the nature of the anion of the quinolinium salt.

Monomeric 1,2-dihydroquinolines were first synthesized by Freund and Richard[3,4] by the reaction of Grignard reagents on quaternary quinolinium salts (I–II),



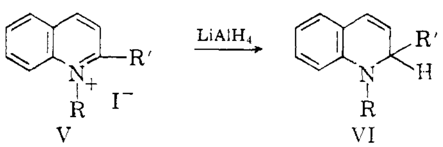
R = alkyl; R′ = H, or alkyl; R″ = alkyl or aryl

Evidence for assignment of the 1,2-dihydroquinoline structure was based chiefly on the formation of *N*-benzoyl-*N*-methylanthranilic acid (IV) when the product (III) of the reaction of quinoline methiodide with phenylmagnesium bromide was oxidized with calcium permanganate.



The chemistry of these substances has been studied further by Meisenheimer and co-workers.[5,6] As will be presented in a subsequent communication, choice of III for definitive proof of structure of the products of the Freund reaction as a group was somewhat unfortunate.

In 1949 Schmid and Karrer[7] described the formation of 1,2-dihydroquinoline derivatives by reduction of 1-alkyl-2-substituted quinolinium iodides with lithium aluminum hydride (V–VI),



R = alkyl; R′ = H, alkyl or aryl

They expressed doubt concerning the validity of the structure assignments for Freund's dihydroquinolines. It was noted that the dihydroquinolines produced by lithium aluminum hydride reduction rapidly lost their reducing power when exposed briefly to strong acid and it was suggested that, inasmuch as Freund had used hydrochloric acid during the work-up of his reaction mixtures, some change may have been effected on the initial products of the reactions. Further, the properties reported by Schmid and Karrer for their compounds were stated to differ somewhat from those of the dihydroquinolines made by the Freund reaction.

In connection with work presently under way in these laboratories, procurement of 1,2-dihydroquinolines of unequivocal structure was necessary. Therefore, in view of the contradictory statements appearing in the literature, an exhaustive study of these interesting and relatively unstable substances was undertaken. The present communication deals with dihydroquinolines prepared by metal hydride reduction of quaternary quinolinium salts. Results of a study of the Freund reaction will be presented in a subsequent communication.

At the outset 1-methylquinolinium iodide (VII) was subjected to the Freund reaction with phenylmagnesium bromide and 2-phenylquinoline methiodide (VIII) was reduced with lithium aluminum hydride in ether. Use of strong mineral acids was avoided in the manipulation of the products of both reactions. If 1,2-dihydroquinolines are indeed formed in the Freund reaction, then the same

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[1] The material presented is taken from a dissertation submitted by Bruce H. Wark in partial fulfillment of the requirements for the Ph.D. degree, University of Michigan.

[2] Visking Division of Union Carbide Corp. Fellow, 1958.

[3] M. Freund, *Ber.*, **37**, 4666 (1904).

[4] M. Freund and L. Richard, *Ber.*, **42**, 1101 (1909).

[5] J. Meisenheimer and M. Schutze, *Ber.*, **56**, 1353 (1923).

[6] J. Meisenheimer, E. Stotz, and K. Bauer, *Ber.*, **58**, 2826 (1925).

[7] H. Schmid and P. Karrer, *Helv. Chim. Acta*, **32** 960 (1949).