molecular wave functions through a variable electronegativity self-consistent field (VESCF) treatment[10] of the atomic orbitals, then the use of a linear combination of these orbitals (LCAO) to build the ground and excited configuration wave equations, which are finally solved to give the state energies and orbitals. The transitions then result directly from the differences between the energies, and the oscillator strengths are derived from the orbitals.

The LCAO–VESCF orbitals are obtained from the diagonalization of a Hartree–Fock SCF matrix by an iterative procedure, which minimizes the energy of the ground state (V_0).

All computations were carried out on an IBM 7074 computer. For the largest molecules studied, seven atomic orbitals are used. They lead to a configuration interaction matrix of order 91 which is always factored as much as possible before diagonalization. The total computation time for such a molecule is about 20 min.

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pK's of 1,1-Dinitro Compounds and Conformations of Dinitrocarbanions

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Received November 10, 1967

Abstract: pK's in the series $RC(NO_2)_2H$ are related to inductive effects of nonconjugating substituents R through the expression, pK = 5.24–3.60σ^*. Acidities in this series are highly dependent on the steric requirements of R. Rationales for deviations of individual dinitro compounds from the ρ^*–σ^* relationship are based on changing conformations in the conjugate dinitrocarbanions.

Most of the existing information regarding pK's of 1,1-dinitroalkanes, $RC(NO_2)_2H$, has been reported in a series of papers by Novikov and coworkers.[1–4] In the course of a continuing study of how substituents affect properties and reactivities of dinitrocarbanions,[5–8] we have had occasion to repeat some of these measurements and to determine the ionization constants of a number of additional 1,1-dinitro compounds. Although our pK values for specific materials (dinitromethane and 1,1-dinitroethane) agreed well with data reported by the earlier investigators, we have arrived at somewhat different conclusions regarding the magnitude of substituent effects in this series.

In their most recent communication on the subject,[4] the earlier workers had suggested that dissociation constants of $RC(NO_2)_2H$ were related to Taft's σ^* values[9] of nonconjugated substituents R through the expression

$$pK = 5.22 - 1.74\sigma^* \qquad (1)$$

Of the 14 compounds cited (I, II, IIIa–d, IVa–d, V–VII, and XVIII of Table I), measured pK's for 11 differed by less than 0.2 pK unit from predictions by eq 1, and arguments based on both steric and electronic considerations were enlisted to account for the "dropout" of the other three (VI, VII, and XVIII).

We have found, however, that in the cases of three additional pK's reported by Novikov and coworkers for which the σ^*'s of R are now known or can be inferred[10] (VIII–X) and for seven pK's determined in the present investigation (XI–XVII), eq 1 gives poor to unacceptable agreement with measured values. These experimental pK's and the corresponding Δ's ($\Delta = pK_{\text{found}} - pK_{\text{calcd}}$) are assembled in Table I together with the earlier data.

We have applied standard least-squares treatments[11] (discussed in detail in the Appendix) to the data in Table I, appropriately weighted, to arrive at the following equation relating pK's of $RC(NO_2)_2H$ compounds (unbranched in the 2 position, see below) to σ^* values of nonconjugating R's:

$$pK\,(\text{in } H_2O \text{ at } 25°) = 5.24 - 3.60\sigma^* \qquad (2)$$

Although pK_0 in this expression is about the same as suggested by the earlier workers, the value of ρ^* is more than doubled.

This new equation accommodates the total body of experimental information far better than the old, the

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(1) S. S. Novikov, V. M. Belikov, A. A. Fainzil'berg, L. V. Ershova, V. I. Slovetskii, and S. A. Shevelev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1855 (1959).

(2) S. S. Novikov, V. I. Slovetskii, V. M. Belikov, I. M. Zavilovich, and L. V. Epishina, *ibid.*, 520 (1962).

(3) S. S. Novikov, V. I. Slovetskii, S. A. Shevelev, and A. A. Fainzil'berg, *ibid.*, 598 (1962).

(4) V. I. Slovetskii, S. A. Shevelev, V. I. Erashko, L. I. Biryukova, A. A. Fainzil'berg, and S. S. Novikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 655 (1966).

(5) M. J. Kamlet, R. E. Oesterling, and H. G. Adolph, *J. Chem. Soc.*, 5838 (1965).

(6) H. G. Adolph and M. J. Kamlet, *J. Am. Chem. Soc.*, **88**, 4761 (1966).

(7) M. J. Kamlet and D. J. Glover, *Tetrahedron Letters*, No. 27, 17 (1960).

(8) M. J. Kamlet and D. J. Glover, *J. Org. Chem.* 27, 537 (1962).

(9) R. W. Taft, Jr., in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13.

(10) A σ^* value of 0.99 for $CH_3C(NO_2)_2CH_2$ was obtained by applying the normal 2.8 quenching factor to σ^* = 0.352 for $CH_3C(NO_2)_2CH_2$-CH_2 as determined by J. Hine and N. C. Bailey, Jr. [*J. Org. Chem.*, **26**, 2098 (1961)], from the reaction of 4,4-dinitrovaleric acid with diphenyldiazomethane. Substituting H for CH_3 and again applying the normal quenching factor led to σ^* = 1.05 for $CH(NO_2)_2CH_2$.

(11) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

Table I. Ionization Constants of 1,1-Dinitro Compounds, $RC(NO_2)_2H$, at 25°

No.	Substituent, R	$\sigma^{*\,a}$	pK_{found}	ΔpK (found − calcd)		Source of data
				Eq 1	Eq 2	
I	CH_3	0.000	5.13	−0.01	−0.07	*b*
			5.13			*c*
			5.17			*d, e*
II	CH_3CH_2	−0.100	5.49	+0.14	−0.11	*d, e*
IIIa	$CH_3CH_2CH_2$	−0.115	5.35	−0.04	−0.30	*d, e*
		(−0.120)^f				
IIIb	$(CH_3)_2CHCH_2$	−0.125	5.36	−0.06	−0.33	*g, e*
		(−0.139)^f				
IIIc	$CH_3(CH_2)_2CH_2$	−0.130	5.34	−0.06	−0.37	*h, e*
IIId	$CH_3(CH_2)_3CH_2$	−0.126	5.37	−0.03	−0.32	*h, e*
IVa	$CH_3(CH_2)_4CH_2$	−0.126	5.46	+0.06	−0.23	*g, e*
IVb	$CH_3(CH_2)_5CH_2$	−0.126	5.46	+0.06	−0.23	*g, e*
IVc	$CH_3(CH_2)_6CH_2$	−0.126	5.46	+0.06	−0.23	*g, e*
IVd	$CH_3(CH_2)_7CH_2$	−0.126	5.45	+0.04	−0.24	*h, e*
V	$CH_2{=}CHCH_2$	+0.13^k	4.95	+0.18	+0.18	*i*
		(+0.233)^f				
VI	$HOCH_2CH_2$	+0.198	4.44	−0.35	−0.09	*i*
VII	H	+0.490	3.57 (3.87)^j	(−0.77)^p	+0.39	*o*
VIII	C_6H_5	+0.60	3.71	−0.43	+0.63	*l*
IX	$CH(NO_2)_2CH_2$	+1.05^m	1.09 (1.39)^n	−2.00	−0.07	*d, e*
X	$CH_3C(NO_2)_2CH_2$	+0.99^m	1.35	−2.15	−0.33	*d, e*
XI	$CH_3OOCCH_2CH_2$	+0.255	4.34	−0.44	+0.02	*b*
XII	CH_3OCH_2	+0.52	3.48	−0.80	+0.11	*b*
XIII	$N{\equiv}CCH_2CH_2$	+0.465	3.45	−1.06	−0.12	*b*
XIV	$O_2NCH_2CH_2$	+0.50	3.24	−1.11	−0.20	*b*
XV	CH_3OOCCH_2	+0.71	3.08	−0.90	+0.40	*b*
XVI	$(CH_3)_3\overset{+}{N}CH_2$	+1.90	−1.87	−3.79	−0.27	*b*
XVII	$N{\equiv}CCH_2$	+1.30	2.27	−0.69	+1.71	*b*
XVIII	$(CH_3)_2CH$	−0.190	6.71	+1.20	+0.79	*g, e*
			Av^q	(±0.66)	(±0.30)	

[a] Reference 9. [b] Present investigation. [c] Reference 21. [d] Reference 3. [e] Estimated either by interpolation from 20 and 40° values in the reference cited or by assuming temperature effect on 20° value parallels that for closely related compounds. In most instances the correction involves subtracting 0.03 to 0.05 pK unit from 20° value. [f] σ^*'s in parentheses are those used in the least-squares fit leading to eq 1. [g] Reference 1. [h] Reference 2. [i] Reference 4. [j] This is the value used in the correlation leading to eq 2; 0.30 pK unit added to account for two equivalent ionizable protons; see text and ref 29. [k] σ^* value used is same as for $CH_3CH{=}CHCH_2$. [l] Private communication, Professor S. S. Novikov, Zelinskii Institute, Moscow. [m] Reference 10. [n] Value used in correlation leading to eq 2; two equivalent ionizable protons. [o] Reference 6. [p] Δ value reported by Novikov based on unadjusted pK; adding the 0.30 factor would lead to Δ = −0.44. [q] Excluding compound XVIII; see text.

average Δ value being ±0.30 pK unit for eq 2 over an extended σ^* range compared with $\Delta_{\text{av}} = \pm 0.66$ for eq 1.[12] Comparing regression lines in Figure 1, wherein pK values are plotted against σ^*'s, allows a more convenient evaluation of these two expressions relative to individual data points.

Comparison of ρ^* with Other Ionizations. Comparison with inductive substituent effects in other ionizations also provides a basis for preferring the new ρ^* value. Although accurate prediction of ρ^* from first principles is not yet possible, it seems reasonable that in ionizations the magnitude of ρ^* will depend on the number of atoms separating R from the dissociating proton and the nature of these insulating atoms. Where R is once removed from the atom bearing the ionizing proton, ρ^*'s are in the order of 1.5 ± 0.3, *e.g.*, pK's of RCOOH,[13] $\rho^* = 1.72$; acidities of RCH_2OH,[14] $\rho^* = 1.36$.

As might be expected, higher ρ^*'s are recorded where R is directly affixed to the atom bearing the ionizing proton. Thus for RNH_2, R_2NH, and R_3N basicities[15] the ρ^* values are 3.14, 3.23, and 3.30, respectively, and for RPH_2, R_2PH, and R_3P base strengths[16] ρ^* values are 2.64, 2.61, and 2.67. Since $RC(NO_2)_2H$ ionizations fall into this latter category, $\rho^* = 3.60$ does not appear out of line.

Steric and Conformational Effects on p*K*. Taft has suggested[17] that some variable or variables other than the pure inductive effect of R must be considered as contributory where vertical deviations from correlation lines in ρ^*–σ^* relationships exceed 0.16 ρ^* unit (0.58 pK unit in the current instance). Of the 24 pK's in Table I, those for 2-methyl-1,1-dinitropropane (XVIII), phenyldinitromethane (VIII), and 3,3-dinitropropionitrile (XVII) must by this criterion be considered not to conform with the linear free energy–polar energy relationship.

The failure of eq 2 was not unexpected in the case of R = $(CH_3)_2CH$, since the marked acid-weakening effect of branching in the 2 position of 1,1-dinitroalkanes had already been observed by Shechter and coworkers[18] in the early 1950's. They had determined pK's in

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[12] A sounder statistical basis for preferring eq 2 is in the very much higher correlation coefficient; see Appendix.

[13] Reference 9, Table IX, reaction 3.

[14] J. Hine and M. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952); ref 9, Table IX, reaction 8.

[15] H. K. Hall, Jr., *J. Am. Chem. Soc.*, **79**, 5441 (1957).

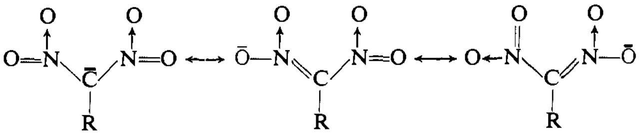
[16] W. M. Henderson, Jr., C. A. Streuli, and S. A. Buckler, *ibid.*, **82**, 5791 (1960).

[17] Reference 9, p 621.

[18] Private communication, Professor Harold Shechter, The Ohio State University. The pK's were measured by Drs. D. Brain, R. Kaplan, and T. Moritsugu. It is worth pointing out that the pK difference between II and XVIII in 44% methanol as measured by Shechter, *et al.*, corresponds almost exactly to that in water as determined by Novikov, *et al.*

44% methanol at 25° to be as follows: II, 6.21; XVIII, 7.42; $(CH_3)_3CC(NO_2)_2H$, 8.77. Novikov and coworkers[4] had also commented on this effect, attributing the "dropout" of XVIII to the fact that "the steric factor, associated with the carbon skeleton, changes substantially." This extreme sensitivity of 1,1-dinitroalkane acidities to steric effects, which served as the basis for our restricting eq 2 to $RC(NO_2)_2H$ compounds *unbranched at the 2 position*, deserves discussion.

1,1-Dinitroalkane acidities depend most strongly on the stabilities of the corresponding conjugate dinitrocarbanions which, in turn, are governed primarily by contributions of canonical structures XIXa–c to the resonance hybrid. Kamlet and Glover[8] have suggested that oxygen–oxygen repulsions in most 1,1-dinitrocarbanions would impart a tendency toward skewing of the C–N(–O)–O planes from the R–C(–N)–N planes, in consequence of which, resonance contributions of the individual nitro groups in the preferred conformations would be less than in totally coplanar situations. Where steric considerations allowed, an alternative mechanism for relief of O–O repulsions would involve spreading of the N–C–N angle from the normal 120°, with corresponding contraction of the R–C–N angles. Such an effect, by increasing the O–O distances, would allow lesser nitro group skews in the preferred conformation than would be the case if the N–C–N angle were 120°.



XIXa XIXb (two equivalent structures) XIXc (two equivalent structures)

This provides a rationale for the extreme sensitivity of dinitroalkane acidities to steric factors, since it follows that the greater the steric requirements of R in $RC(NO_2)_2^-$, the more difficult it becomes to contract the R–C–N angles and expand the N–C–N angle. The O–O repulsions manifest themselves in greater angles of skew of the C–N(–O)–O planes from the R–C(–N)–N plane, and lesser contributions of canonical structures XIXb and XIXc to the stability of the dinitrocarbanion resonance hybrid are realized.

Such skewing, induced by O–O repulsions, would also serve to account for much of the "saturation effect" noted by Pearson and Dillon in the p*K*'s of the polynitromethanes but not with the polycyanomethanes,[19] *i.e.*

	p*K*		p*K*
CH_4	40		
CH_3NO_2	11	CH_3CN	25
$CH_2(NO_2)_2$	4	$CH_2(CN)_2$	12
$CH(NO_2)_3$	0	$CH(CN)_3$	0 (−5[20])

The linear cyano groups exert fully additive resonance effects in all cases, but the nitro groups exert fractionally smaller resonance effects as the degree of substitution and the consequent extent of skewing increases. Dinitroacetonitrile, wherein the linear cyano group allows greater coplanarity of the nitros than in nitroform, shows p*K* = −6.2.[21]

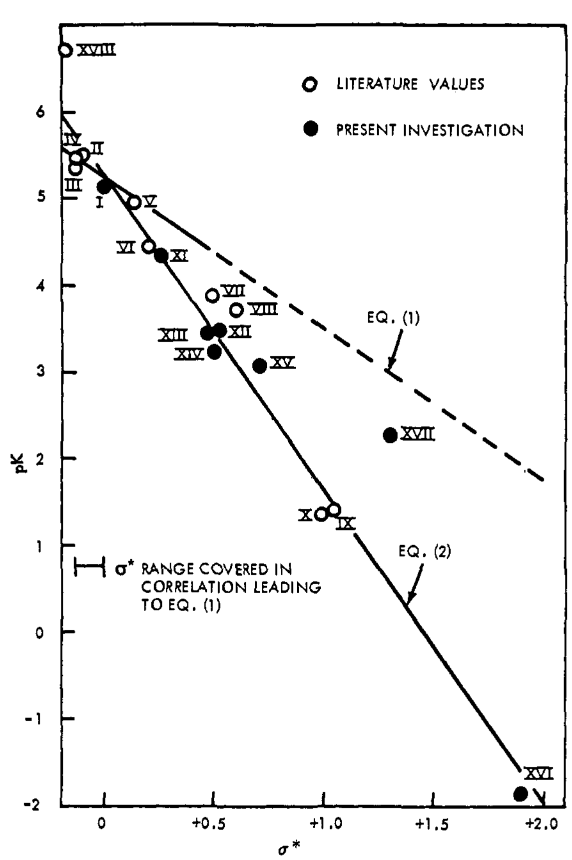


Figure 1. Variation of p*K* with σ* for $RC(NO_2)_2H$.

Novikov and coworkers[4] have questioned the role played by expansion of the N–C–N angle because "in sterically hindered molecules a rotation of the voluminous groups around ordinary bonds occurs preferentially over a change in the lengths of these bonds or a change in the valence angles." This alternative viewpoint is based on a generalization by Kitaigorodskii[22] which is probably reasonably valid in relatively nonpolar systems.

Since this seems to be a pivotal question in attempts to unravel the effects of substituents on properties and reactivity, not only of dinitrocarbanions, but of a variety of highly conjugated molecules, we consider it worth mentioning that evidence is now available which indicates that, in the crystal phase at least, Kitaigorodskii's dictum does not necessarily apply to such systems. Highly resonance stablilized molecules will undergo appreciable changes from normal bond lengths and bond angles in order to maximize resonance interactions. As concerns bond lengths, for example, a total structure determination on 1,3,5-triamino-2,4,6-trinitrobenzene[23] has shown appreciable increases from normal aromatic C–C distances in order to allow all atoms in the molecule to remain essentially coplanar.

More immediately to the point, a recent total structure determination on the hydrazinium salt of nitroform[24] strongly substantiates the Kamlet–Glover hypothesis as concerns both angles of skew and N–C–N angles. The crystal of this material contains two independent anions (A and B) whose differences arise

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(19) R. G. Pearson, and R. L. Dillon, *J. Am. Chem. Soc.*, **75**, 2439 (1953).

(20) R. H. Boyd, *ibid.*, **83**, 4288 (1961).

(21) T. N. Hall, *J. Org. Chem.*, **29**, 3587 (1964).

(22) A. I. Kitaigorodskii, *Tetrahedron*, **9**, 183 (1960).

(23) H. H. Cady and A. C. Larson, *Acta Cryst.*, **18**, 495 (1965).

(24) B. Dickens, *Chem. Commun.*, 242 (1967).

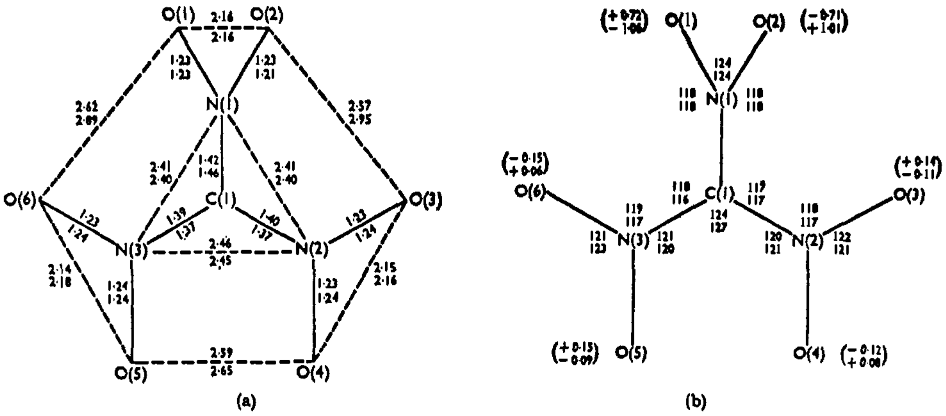

Figure 2. The structure of the nitroform anions in hydrazine nitroform. The upper numerals refer to anion A, the lower ones to anion B. (a) Distances in angstroms. (b) Angles (degrees) and displacements (angstroms) from the C(1)-N(1)-N(2)-N(3) plane. Taken from Dickens.[24]

from packing and hydrogen-bonding forces. Each anion contains two essentially equivalent slightly skewed nitro groups and one highly skewed nitro group; dihedral angles from an accurate N-C(-N)-N plane are 7, 8, and 41° in A; 4, 5, and 74° in B. Comparing the two anions, it is seen that the greater the dihedral angle of the highly skewed nitro, the less are the dihedral angles of the closer-to-coplanar nitros.

Furthermore, and more important, the N-C-N bond angles in both anions differ significantly from 120°. Taking N(1) as the nitrogen of the highly skewed nitro group, the observed bond angles are as follows:

	A	B
N(1)-C-N(2)	117°	117°
N(1)-C-N(3)	118°	116°
N(2)-C-N(3)	124°	127°

Thus, the greater the angles between any C-N bond and its neighbors, the less is the angle of skew of the nitro group from the N-C(-N)-N plane. This structure, pictured in Figure 2, is in complete accord with the viewpoint presented in the present paper[25] and at variance with that propounded by Novikov and Kitaigorodskii.

The Other Out-of-Line p*K*'s. Phenyldinitromethane (VIII) was included in the present correlation on the basis of an earlier observation by Kamlet and Glover.[8] These workers had correlated ultraviolet absorption maxima of $RC(NO_2)_2^-$ salts with σ^* of R through the expression

$$\lambda_{\max} = (381.6 - 15.25\sigma^* - 8.5\,\gamma)\ \mathrm{m}\mu \qquad (3)$$

where γ is 1.0 or 0.0 depending on the presence or absence of nonbonded electrons on the atom β to the dinitromethide function. Finding that $\lambda_{\max}$ for VIII was within 0.5 mμ of the position predicted from eq 3, they concluded that the angle of twist of the ring from the C-C(-N)-N plane necessarily approached 90° and that the phenyl group exerted a purely inductomeric effect.

The p*K* results are consistent with this conclusion. If any significant proportion of the carbanion charge were delocalized to the ring through resonance interactions, one would anticipate a lower p*K* than called for by eq 2. The +0.63 unit difference between observed and predicted p*K*'s (Δ in Table I) is in the opposite direction.

It is possible to rationalize this positive Δ value on the basis that the ring's π electrons exert a repulsive force on the nitro oxygens, so that a field effect rather than steric influences would here cause increased skewing of the nitro groups and contraction of the N-C-N angle. The consequent destabilization of canonical structures XIXb and XIXc would have to be matched by an almost equal destabilization of structure XIXa (possibly by an effect analogous to nonbonded p-π repulsion[26]), however, to account for the good fit of VIII to eq 3.[27]

As with VIII, the salt of 3,3-dinitropropionitrile (XVII) shows $\lambda_{\max}^{H_2O}$ corresponding quite closely to that predicted from eq 3. Here, however, we have no such ready rationale as the above to account for the marked deviation (Δ = +1.71 p*K* units) from eq 2. That this anomalous p*K* is real, and not due to partial decomposition or some other side reaction, seems likely. Spectra of mixtures of free acid and conjugate carbanion used in the determinations showed no fading or other changes with time. Further, p*K*'s were determined starting with the potassium salt and with the free acid. These agreed to within 0.05 p*K* unit.

Although repulsive forces by the π electrons in the cyano group of XVII might account for the sign of Δ, we would hesitate to suggest that they account for the magnitude.[28] Nor is there any *a priori* basis for suggesting increased hydrogen-bonding or differing solvation of the free acid or carbanion relative to other

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(25) It should be emphasized that we consider N-C-N > 120° and skewed nitro groups as probable but not necessary features of dinitrocarbanion conformations. A recent structure determination on potassium 4,4-dinitro-2-butenamide [J. R. Holden and C. Dickinson, *J. Am. Chem. Soc.*, in press] shows all atoms to be essentially coplanar with an N-C(4)-N angle of 120°. Here, however, if one can judge from bond lengths and the position of the cation in the lattice, an appreciable portion of the formal negative charge is delocalized to the carboxamide oxygen, far from the carbanion site. It is also noteworthy that, to allow total coplanarity, the C(2)-C(3)-C(4) angle in this molecule is expanded to 131°.

(26) J. N. Murrell, "The Theory of Electronic Spectra of Organic Molecules", John Wiley and Sons, Inc., New York, N. Y., 1963, Chapters 9 and 10.

(27) To explain substituent effects on spectra, it was suggested[8] that structures XIXa, b, and c were contributors to both electronic ground and electronic excited states, with the electronic excited state "partaking more" of structures XIXb and c, *i.e.*, an electron drift away from carbon in the transition.

(28) It may be noted that the three compounds with multiple bonds connecting the atoms β and γ to the dinitromethide function (V, XV, and XVII) all show positive Δ values.

1,1-dinitro compounds. The infrared spectrum of the potassium salt shows no unusual or distinguishing features such as might imply markedly changed hybridization in the carbanion.[5] We must therefore leave the question of the anomalous p*K* of XVII unresolved at the present writing and will welcome any suggestions in this regard.

Dinitromethane (VII). Based on ionization data then available, earlier workers[4,8] had concluded that VII was a stronger acid than would be expected only from inductive differences between hydrogen and alkyl. Kamlet and Glover[8] had attributed this "enhanced acidity" to an expanded N–C–N angle and increased nitro group coplanarity in dinitromethide relative to other dinitrocarbanions. With the higher ρ^* value found in the present investigation, the conclusion regarding the acidity of VII no longer appears to be valid. Dinitromethane is a weaker acid than would be predicted from eq 2 by 0.39 p*K* unit if a statistical factor (+0.30 p*K* unit) is applied to account for the two equivalent ionizable protons, by 0.09 p*K* unit if this statistical factor is not used.[29]

A priori considerations would still lead us to believe that dinitromethide approaches coplanarity more closely than the other dinitrocarbanions; indeed, such is an almost necessary consequence of the arguments offered above to explain steric effects on p*K*. It therefore becomes necessary to invoke some offsetting, acid-weakening effect, which operates only in the specific instance of VII, to account for the close-to-normal p*K*. Such a specific effect might, for example, arise from increased solvation leading to greater stabilization of the un-ionized species, which is sterically more accessible to solvent only in this instance.

3,3-Dinitropropanol (VI) also deserves comment in connection with possible secondary effects on p*K*. Novikov and coworkers[4] had rationalized enhanced acidity of VI ($\Delta = -0.35$ p*K* unit relative to prediction from eq 1) to stabilization of the anion by a hydrogen bond. Equation 2 does not rule out such an effect, but suggests that its magnitude may be smaller ($\Delta = -0.09$).

σ^* Values. The p*K* reported for 1,1,3,3-tetranitrobutane (X), and less directly that for the first ionization of 1,1,3,3-tetranitropropane (IX), lend support to $\sigma^* = +0.352$ for the 3,3-dinitrobutyl group as suggested by Hine and Bailey.[10] Equation 2 leads to $\sigma^* = +1.08$ for $CH_3C(NO_2)_2CH_2$, and hence $\sigma^* = +0.38$ for $CH_3C(NO_2)_2CH_2CH_2$. Fauth, Richardson, and Nauflett[30] have recently reported that 4,4-dinitrovaleric acid has p*K* = 3.98, which leads[13] to $\sigma^* = +0.39$ for 3,3-dinitrobutyl.

The σ^* value of 2-nitroethyl has also been the subject of some recent discussion. From the p*K* of nitroacetic acid, Slovetskii and Fainzil'berg[31] have arrived at $\sigma^* = +1.73$ for NO_2CH_2, and hence $\sigma^* = +0.62$ for $NO_2CH_2CH_2$, in place of the currently accepted[9] +1.40 and +0.50. The p*K* of 1,1,3-trinitropropane (XIV), taken with eq 2, leads to an intermediate value for $NO_2CH_2CH_2$, *i.e.*, $\sigma^* = +0.55$.

Ultraviolet Spectra. Some additional spectral data for potassium salts of compounds listed in Table I allow a further test of Kamlet and Glover's λ_{max}-σ^* relationship given by eq 3.[8] These new data are assembled in Table II, together with results of our present measurements on trimethylammonium N-(2-nitroethyl-2-nitronate) (XVI). In the latter case, our ϵ_{max} differed significantly from the reported value.[32] For all other compounds studied, the spectra agreed with literature values[8] to within 0.5 mμ and 0.01 log ε unit. Also, as best as one can judge from a small-scale reproduction of the spectrum,[3] λ_{max} for $CH_3C(NO_2)_2CH_2C(NO_2)_2^-K^+$ lies close to the 366.5-mμ value required by eq 3.

Table II. Absorption Spectra of $RC(NO_2)_2^-K^+$

	$\lambda_{max}^{dil.\ NaOH}$, mμ		
Substituent, R	Eq 3	Found	Log ε
CH_3OOCCH_2	370.8	371	4.27[a]
CH_3OCH_2	365.2	365.5	4.24[a,b]
$N{\equiv}CCH_2CH_2$	374.5	374	4.24[a]
$CH_2{=}CHCH_2$	379.6	379	4.22[c]
$HOCH_2CH_2$	378.5	379	4.18[c]
$(CH_3)_3\overset{+}{N}CH_2$	352.6	352	4.23[a] (lit. 4.17[d])

[a] Present investigation. [b] Fades on standing; see Experimental Section. [c] Private communication, Professor S. S. Novikov, Zelinskii Institute, Moscow. [d] Reference 32.

Experimental Section

Trimethylammonium N-(2-nitroethyl-2-nitronate)[32] and the potassium salts of methyl 4,4-dinitrobutyrate,[33] 1,1-dinitroethane,[33] 4,4-dinitrobutyronitrile,[33] methyl 2,2-dinitroethyl ether,[34] 1,1,3-trinitropropane,[35] and 3,3-dinitropropionitrile[36] were prepared and purified according to literature methods. Methyl 3,3-dinitropropionate, prepared by the procedure of Meisenheimer,[36] was found to be a mixture of the ester, the corresponding amide, and a small amount of an unidentified product. Removal of the amide by chromatography on silica, followed by formation of the potassium salt and crystallization from warm methanol, gave pure potassium methyl 3,3-dinitropropionate.

The p*K*'s were determined spectrophotometrically at 25.0 ± 0.1° in phthalate buffers of ionic strength 0.05 ± 0.005 using a Cary Model 14 recording spectrophotometer. The determinations required the measurement of the pH's and the absorbances of buffered solutions of the potassium salts at or near λ_{max}. Calculations were by the equation, $pK = pH - \log (A - A_1)/(A_2 - A)$; A = absorbance of a given concentration of salt at a measured pH, A_1 = absorbance of the free acid at the same concentration, A_2 = absorbance of the completely dissociated acid at the same concentration.[37] The pH's of the solutions, except those of XVI, were measured with a Beckman Model G pH meter and agreed with calculated values. The p*K* of the trimethylammonium derivative, XVI, was sufficiently low that the acidity function, H_0, for hydrochloric acid solutions was employed[38]; $pK = H_0 - \log ([B]/[BH^+])$, where [B] and [BH+] are the concentrations of the unprotonated and protonated forms, respectively.

All p*K*'s reported in the present investigation represent averages of three measurements at three pH's. These generally agreed to within 0.03 p*K* unit. Because the p*K* found for potassium 3,3-

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(29) Whether the statistical factor should be applied where the equivalent ionizable protons are on the same carbon atom is not clearly resolved. The decision to use the +0.30 p*K* unit "correction," even though it caused poorer correlation to the equation, was based on arguments by S. W. Benson, *J. Am. Chem. Soc.*, **80**, 5151 (1958).

(30) M. I. Fauth, A. C. Richardson, and G. W. Nauflett, *Anal. Chem.*, **38**, 1947 (1966).

(31) V. I. Slovetskii and A. A. Fainzil'berg, *Zh. Org. Khim.*, 2, 1488 (1966).

(32) L. Zeldin and H. Schechter, *J. Am. Chem. Soc.*, **79**, 4708 (1957).

(33) D. J. Glover and M. K. Kamlet, *J. Org. Chem.*, **26**, 4734 (1961).

(34) J. Meisenheimer, *Ber.*, **36**, 434 (1903).

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

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

(37) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1965, pp 560–72.

(38) M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 12 (1957).

dinitropropionitrile did not correspond to the predicted value, a further determination was carried out using the free acid,[36] which was purified by chromatography on silica. The observed p*K* agreed to within 0.05 unit with that obtained from the potassium salt.

In the case of methyl 2,2-dinitroethyl ether, the buffered solutions showed decreasing absorbances on standing. Extrapolations of plots of optical density *vs.* time were used to determine initial absorbances of these solutions.

Acknowledgments. The authors are indebted to Dr. L. A. Kaplan and Mr. N. Burlinson for making available to us samples of the potassium salts of XIII and XIV. We also wish to thank Professor S. S. Novikov of the Zelinskii Institute of Organic Chemistry, Soviet Academy of Sciences, Moscow, for providing us with unpublished information regarding the p*K* of VIII and the spectra of V and VI. The work was carried out under an NOL Foundational Research task.

Appendix

Least-Squares Treatments. Our first attempt at relating p*K*'s to σ^*'s involved a standard least-squares treatment[11] of 23 data points in Table I (excluding XVIII which was branched at the 2 position, see text). This led to

$$pK = 5.11 - 3.24\sigma^* \qquad (4)$$

where r (the correlation coefficient) = 0.975 and s (the standard deviation) = 0.422. Because Δ for 3,3-dinitropropionitrile (XVII) was more than four times the average for the other materials, and because it was considered that some extraneous unexplained factor was operating in this instance (see text), XVII was excluded from the next trial, which involved a 22-point fit. This gave the expression

$$pK = 5.12 - 3.48\sigma^*$$

where

$$r = 0.990, s = 0.271 \qquad (5)$$

Although correlation of the experimental information to eq 5 was excellent by Jaffé's criteria,[11] it was recognized that the treatment leading to this expression had placed undue weight on a large number of almost identical p*K* values for almost identical compounds with almost identical σ^*'s. A next trial therefore involved using single values for compounds IIIa–d ($pK_{av} = 5.36$, $\sigma^*_{av} = -0.126$) and IVa–d ($pK_{av} = 5.46$, $\sigma^*_{av} = -0.126$). The resulting 16-point least-squares fit led to eq 2, $r = 0.990$, $s = 0.292$.

Because of the difference between our own conclusions and those reported by the Novikov group, and because the p*K*'s reported by these earlier workers fit eq 2 at least as well as did our own data, we repeated the least-squares treatment which they had used to arrive at eq 1, a ten-point fit based on the dinitroalkanes I–IV. This combination involved a spread in p*K*'s of only 0.32 and a spread in σ^*'s of only 0.14 unit. For nine of the ten compounds the p*K* spread was 0.14 and the σ^* spread 0.04. For comparison, a 0.1-unit accuracy was claimed[4] for the experimental determination of the p*K*'s.

In consequence of the small spreads in σ^* and p*K*, some of the quantities involved in the standard least-squares treatment were also quite small and, depending on how the numbers were "rounded off," the results ranged from

$$pK = 5.24 - 1.69\sigma^*$$
$$(r = 0.726, s = 0.069)$$

to

$$pK = 5.22 - 1.76\sigma^*$$
$$(r - 0.760, s = 0.064)$$

which bracket the values of pK_0 and ρ^* in eq 1. Statistical correlation of the ten data points to eq 1 was quite poor and, from the r value, represents violation of a ρ–σ relationship by Jaffé's criteria ($r < 0.9$ unsatisfactory where $\rho > 1$).[11]

It may have been that the earlier workers were misled by the small differences between found and predicted p*K*'s for the compounds fitted to eq 1, $\Delta_{av} = \pm 0.06$, and that they failed to consider that this Δ_{av} represented almost half the p*K* range covered by nine of the ten compounds in their correlation. Statistical correlation would have been no poorer if the Δ_{av} were 25 times as large over the 7.4-unit range of p*K*'s in the present study. This should emphasize the pitfalls that are inherent in limited-range ρ–σ relationships.