Ultraviolet Spectra of Anions of Mononitro Compounds[1]

FRANCIS T. WILLIAMS, JR.,[2] PAT W. K. FLANAGAN, WILLIAM J. TAYLOR, AND HAROLD SHECHTER

The Chemistry Departments of The Ohio State University, Columbus, Ohio, and Antioch College, Yellow Springs, Ohio

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The ultraviolet absorption spectra of the anions derived from representative primary and secondary nitroalkanes, cycloalkylnitromethanes, nitrocycloalkanes, and various β,γ-nitroalkenes have been investigated. The anions of all exhibited broad, intense absorption bands ($\epsilon_{max} \geqslant 9000$) with maxima between 223 and 284 mμ. The variations in the wave lengths of maximum absorption with structure have been interpreted with reference to a model for the methanenitronate anion suggested by a simple molecular orbital calculation.

Results and Discussion

Nitroalkanes and nitrocycloalkanes exhibit ultraviolet absorption bands at 260–284 and near 200 mμ: the more convenient band suffers the disadvantage that it is not intense (ϵ_{max} ~15–45).[3] In contrast, aqueous solutions of salts of nitromethane,[3a] 2-methyl-3-nitropropene,[4a] and phenylnitromethane[4] have been reported to absorb strongly at 232 mμ (ϵ_{max} 7900), 280 (15,500), and 291 (11,950), respectively. Since the intense and convenient absorption of anions of nitro compounds may allow their identification and analysis, the spectra of salts of representative primary and secondary nitroalkanes, cycloalkylnitromethanes, nitrocycloalkanes, and various β,γ-nitroalkenes have been investigated.

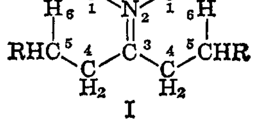
The anions of nitroalkanes absorb strongly at wave lengths above 200 mμ. The absorption bands are broad and intense (ϵ_{max} ~10,000) with maxima in the 223–235-mμ range (Figure 1). Substituted nitromethane anions containing alicyclic substituents (cyclobutyl, etc.) exhibit maxima at slightly longer wave lengths. Nitrocycloalkane anions absorb in the same region as other secondary nitroalkane anions. The anions of nitroalkenes absorb more intensely (ϵ_{max} >15,000) at longer wave lengths with maxima from 276 to 284 mμ. The results are tabulated in Tables I and II.

It is of interest to correlate the effects of structure on the absorption characteristics of substituted carbonitronates.[5] To assist in this correlation a simple molecular orbital calculation (*vide infra*) for the π-electrons of the methanenitronate anion was made. The calculation indicates that excitation of the methanenitronate anion by 225–235-mμ radiation involves a transfer of negative charge to the carbon atom with concomitant reduction in the C–N π-bond order. Figures 2 and 3 give numerical values for the polarities of the ground and excited states for two choices of the parameter value, *h*, which attempts to correct for the electronegativity differences between the carbon and the nitrogen and oxygen atoms of the methanenitronate ion. The calculations indicate that the direction of charge shift and the reduction in the C–N π-bond order on excitation do not change over a range of *h* values centered about the two chosen for Figures 2 and 3. The numerical values for the polarities and degree of bond-order reduction, of course, change somewhat with changes in *h*.

Assuming that the results of the calculation are qualitatively valid, substitution of electron-donating alkyl groups on the carbonitronate would be expected to stabilize the ground state relative to the excited state. Thus, alkyl substitution should produce hypsochromic shifts. This accounts for the observed order (Table I) of the wave lengths of maximum absorption of the anions: methanenitronate > ethanenitronate > 2-propanenitronate and primary alkanenitronates > secondary alkanenitronates. Conversely, substitution of the electron-withdrawing chlorine atom would be expected to stabilize the excited state relative to the ground state thereby producing a bathochromic shift. Such a bathochromic shift is observed upon comparison of the ethanenitronate and 1-chloroethanenitronate ions.

Changes in the alkyl substituents from methyl to larger and more branched alkyl substituents (*e.g.*, Me, Et, *i*-Pr, *t*-Am) would be expected to produce further hypsochromic shifts if their greater electron-releasing inductive power were the controlling factor. The observed shifts are, however, bathochromic. This order could be taken to indicate that the hyperconjugative electron-releasing power of these groups is the controlling factor. However, the molecular orbital calculation coupled with the examination of molecular models suggests an alternative or additional interpretation for these bathochromic shifts.

Molecular models of alkanenitronate anions indicate that substituents larger than methyl are capable of *cis* interaction with the oxygen atoms (see I). The degree of such interaction would be expected to be roughly proportional to the number and size of the atoms in the 6 position. Such interaction may be sufficient to disallow to some extent the normal coplanarity of the carbonitronate group. Loss of coplanarity would destabilize the ground state relative to the excited



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(2) To whom correspondence should be addressed: Chemistry Department, Antioch College, Yellow Springs, Ohio 45387.

(3) (a) G. Kortum, *Z. physik. Chem.*, **B43**, 271 (1939); *Z. Electrochem.*, **47**, 55 (1941); (b) J. W. Goodeve, *Trans. Faraday Soc.*, **30**, 504 (1934); (c) R. N. Haszeldine, *J. Chem. Soc.*, 2525 (1953); (d) N. S. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1006 (1954); (e) H. E. Ungnade and R. A. Smiley, *J. Org. Chem.*, **21**, 933 (1956); (f) T. Urbanski, *Roczniki Chem.*, **31**, 37 (1957); **33**, 635 (1959).

(4) (a) H. Shechter and J. W. Shepherd, *J. Am. Chem. Soc.*, **76**, 3617 (1954). (b) A. Hantzsch and K. Voigt, *Ber.*, **45**, 85 (1912). (c) Incomplete spectra of salts of other mononitro compounds have been reported[4d]; these data are of minimal value for identifying or analyzing these compounds. (d) E. C. C. Baly and C. H. Desch, *J. Chem. Soc.*, 1747 (1907); E. P. Hedley, *Ber.*, **41**, 1195 (1908).

(5) H. B. Hass and M. L. Bender [*J. Am. Chem. Soc.*, **71**, 1767 (1949)] have suggested that salts of nitroalkanes be named as metal alkanenitronates. As an extension of this system of nomenclature the $>C{=}NO_2^-$ group is described as a carbonitronate.

TABLE I

ULTRAVIOLET ABSORPTION SPECTRA OF ANIONS OF NITRO COMPOUNDS[a] IN WATER

Anions, $RR'CNO_2$, of	R	R'	λ_{max}, mμ	ϵ_{max}	n^{20}D[c]	Lit. n^{20}D[c]
Nitromethane[d]	H	H	232	9,000	1.3816	1.38188[e]
Nitroethane	H	Me	229	9,000	1.3920	1.39193[e]
1-Nitropropane	H	Et	231.5	10,000	1.4015	1.40160[e]
1-Nitrobutane	H	*n*-Pr	232	10,000	1.4106	1.41019[e]
3,3-Dimethyl-1-nitrobutane[f]	H	neo-C_5H_{11}	231.5	9,700	1.4237	
2-Methyl-1-nitropropane[g]	H	*i*-Pr	233.5	9,600	1.4070	1.40642[e]
2,2-Dimethyl-1-nitrobutane	H	*t*-C_5H_{11}	235.5	9,800	1.4275	
Cyclohexylnitromethane[h]	H	*c*-C_6H_{11}	234.5	10,900	1.4635	
Cyclopentylnitromethane[h]	H	*c*-C_5H_9	235	11,000	1.4562	1.4587[i]
Cyclobutylnitromethane[f]	H	*c*-C_4H_7	239	11,600	1.4474	
Cyclopropylnitromethane[f]	H	*c*-C_3H_5	242.5	12,800	1.4383	
2-Nitropropane[j]	Me	Me	223	10,900		
2-Nitropentane[j,k]	Me	*n*-Pr	228	11,100	1.4116	
2-Methyl-3-nitrobutane[j,k]	Me	*i*-Pr	226.5	11,200	1.4149	1.4122 (25°)[l]
2,2-Dimethyl-3-nitrobutane[j]	Me	*t*-Bu	229	(8,600)[m]	Crystallizes at 20°	
4-Nitroheptane[j]	*n*-Pr	*n*-Pr	231	11,100		
1-Cyclopropylnitroethane	Me	*c*-C_3H_5	235	12,900	1.4335	1.4338 (15°)[n]
Dicyclopropylnitromethane	*c*-C_3H_5	*c*-C_3H_5	244	12,000	1.4624	1.4619 (15°)[n]
1-Chloronitroethane[d]	Me	Cl	233	9,650	1.4235	1.4235 (25°)[o]

[a] All compounds (except as noted) on the basis of their physical, spectral, and, in most cases, kinetic[b] properties are of good purity. [b] H. Shechter, P. W. K. Flanagan, J. G. Traynham, and F. T. Williams, Jr., Abstracts, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1959, p. 33P. [c] Refractive indices of the parent nitro compound. [d] Alkaline solutions of the nitro compound are unstable. The spectral determinations were made as rapidly as possible. [e] E. E. Troops, Jr., *J. Phys. Chem.*, **60**, 304 (1956). [f] Not previously reported. See Experimental. [g] Slightly contaminated. [h] Obtained from N. Kornblum. [i] I. Rosanov, *Chem. Zentr.*, **1**, 925 (1916). [j] Samples of J. G. Traynham.[b] [k] Obtained from D. C. Iffland. [l] Ref. 18. [m] Minimal value since subsequent kinetic studies revealed that a 10:1 ratio of base to nitro compound is undoubtedly insufficient to completely neutralize this compound. [n] M. F. Hawthorne, *J. Am. Chem. Soc.*, **79**, 2510 (1957). [o] Ref. 13.

TABLE II

ULTRAVIOLET ABSORPTION SPECTRA OF ANIONS OF NITRO COMPOUNDS[a] IN WATER

Anions of	λ_{max}, mμ[b]	ϵ_{max}[b]	n^{20}D[c]	n^{20}D[c]
Nitrocyclobutane	229 (231)	12,600 (10,300)	1.4453	1.4432[d]
Nitrocyclopentane	226 (228)	13,200 (13,500)	1.4535	1.4540[e]
Nitrocyclohexane	231 (233)	12,100 (12,000)	1.4615	1.4626[f]
Nitrocycloheptane	229 (230)	12,100 (12,900)	1.4723	1.4720[f]
3-Nitropropene[g]	276	18,700	1.4298	
(2-Methyl-2 nitropropene)[h]	280	15,500		
1-Nitromethylcyclopentene	284	17,000	1.4771	1.4788[i]
1-Nitrocyclohexene	278	16,100	1.4863	1.4850 (25°)[j]

[a] All compounds (except as noted) on the basis of their physical and spectral properties are of good purity. [b] Values in parentheses are those observed in 50:50 dioxane–water. [c] Refractive indices of the parent nitro compound. [d] D. C. Iffland, G. X. Griner, M. Koral, F. J. Lotspeich, Z. B. Papanastassiou, and S. M. White, Jr., *J. Am. Chem. Soc.*, **75**, 4044 (1953). [e] N. Kornblum, H. O. Larson, R. K. Blackwood, D. D. Mooberry, E. P. Oliveto, and G. E. Graham, *ibid.*, **78**, 1497 (1956). [f] Ref. 18. [g] Slightly contaminated. [h] Ref. 4a. [i] H. B. Frazer and G. A. R. Kon, *J. Chem. Soc.*, 604 (1934). [j] D. V. Nightingale, F. B. Erickson and J. M. Shackelford, *J. Org. Chem.*, **17**, 1005 (1952).

state since, by the molecular orbital calculation, the π-bond order of the C–N bond is much greater in the ground than in the excited states of these anions. Thus, the bathochromic shifts in passing from methyl to larger and more branched alkyl substituents may be the result of the greater relative importance of strain release on excitation than of enhanced stabilization of ground relative to excited states owing to larger inductive effects.

The larger bathochromic shifts observed with the cyclopropyl substituent compared to other alkyl and cycloalkyl substituents (Table I) may be attributed to its ability to extend conjugation. The cyclobutyl group appears to manifest similar properties but to a lesser degree.

Cycloalkanenitronate ions (Table II) do not exhibit a regular order with respect to ring size for their wave lengths of maximum absorption. The observed order, $C_6 > C_7 \sim C_4 > C_5$ cycloalkanenitronates, is not obviously interpretable in terms of electronic factors. The order is reasonable, however, in terms of greater relative significance of internal strain in the ground states of C_4, C_6, and C_7 than that in C_5. Since excitation of these ions reduces the π-bond order of the exocyclic bond, a measure of rehybridization of the carbonitronate carbon may result. The energy levels of the excited states of the strained C_4, C_6, and C_7 cycloalkanenitronate ions would thus be relatively closer to their ground states than the excited level of the C_5 ion. Strain in the ground state of C_4 is expected to result from internal bond angle deformations: the greater strains in C_6 and C_7 than in C_5 may be correlated with other systems containing exocyclic double bonds and appear to arise from torsional and *cis* interactions.[6]

The large bathochromic displacements of the maxima of the conjugated alkene- and cycloalkenenitronate anions result from the compression of the energy levels normally expected with extension of the π molecular orbital system. Calculation of the molecular orbital energies for the anion of 3-nitropropene

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(6) (a) Physical evidence for greater strains in C_4, C_6, and C_7 than in C_5 cycloalkanenitronate systems has been presented by H. Stone, P. W. K. Flanagan, J. G. Traynham, and H. Shechter [Abstracts, the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1956, p. 82O]; (b) J. E. Kilpatrick, K. S. Pitzer, and R. Spitzer, *J. Am. Chem. Soc.*, **69**, 2483 (1947); (c) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *ibid.*, **73**, 212 (1951); (d) H. C. Brown, J. H. Brewster, and H. Shechter, *ibid.*, **76**, 467 (1954); (e) J. J. Wren, *J. Chem. Soc.*, 2208 (1956); (f) H. Shechter, D. E. Ley, and E. B. Roberson, Jr., *J. Am. Chem. Soc.*, **78**, 4984 (1956).

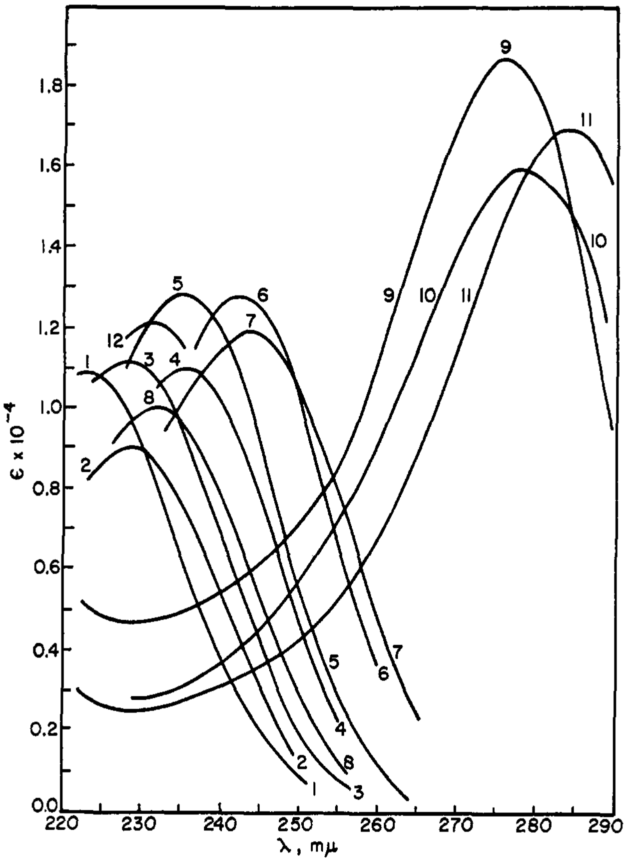


Figure 1.—Ultraviolet absorption spectra for the carbonitronates derived from the following nitro compounds: (1) 2-nitropropane, (2) nitroethane, (3) 2-nitropentane, (4) cyclopentylnitromethane, (5) 1-cyclopropylnitroethane, (6) cyclopropylnitromethane, (7) dicyclopropylnitromethane, (8) 1-nitropropane, (9) 3-nitropropene, (10) 1-cyclohexenylnitromethane, (11) 1-cyclopentenylnitromethane, and (12) nitrocyclohexane.

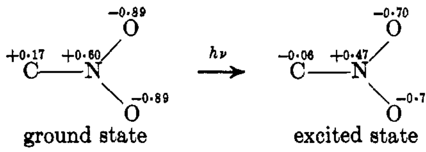


Figure 2.

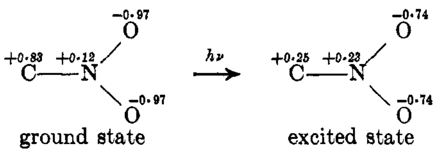
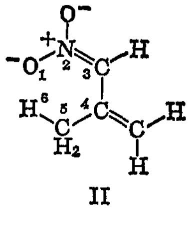


Figure 3.

indicates that the energy of the lowest unoccupied molecular orbital is, as expected, nearer that of the highest occupied orbital than it is in unconjugated alkanenitronates.

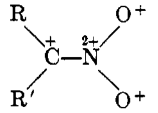
The bathochromic effect observed in the anion of 2-methyl-3-nitropropene on comparison with that of 3-nitropropene may again be associated with *cis* interaction in the former (see II). The bathochromic effect observed in the anion of 1-nitromethylcyclopentene on comparison with that of 1-nitromethylcyclohexene may be associated with greater ring strain in cyclopentenes than in cyclohexenes[6d,7] and in consequent greater strain relief on excitation in cyclopentenes than in cyclohexenes.



II

Molecular Orbital Calculation

A simple molecular orbital calculation of the semiempirical type was carried out in order to obtain semiquantitative values for the changes in atomic charges and bond orders on excitation of an electron of an alkanenitronate. The calculation was effected as follows. The alkanenitronate stripped of its six π-electrons is indicated in III. The 2p π-orbitals



III

were designated as φ_C, φ_N, φ_O and $\varphi_{O'}$. The coulomb integral associated with φ_C was set equal to zero since only the energy difference on excitation of the carbonitronate was of interest. The coulomb integrals α_N, α_O, and $\alpha_{O'}$, associated with φ_N, φ_O, and $\varphi_{O'}$, respectively, were taken as

$$\alpha_N = \alpha_O = \alpha_{O'} = \alpha_C - \delta = -\delta$$

where δ is a positive parameter to be determined. To facilitate calculation, the greater electronegativity of oxygen was presumed to balance exactly the more exposed (doubly charged) nitrogen core. The resonance integrals β_{CN} and β_{NO} were estimated relative to the ethylenic resonance integral $\beta_{CC} = -\beta$, by assuming the same ratios as found for the corresponding overlap integrals by R. S. Mulliken, *et al.*[8] Their values are $S_{CC} = 0.27$, $S_{CN} = 0.24$, and $S_{NO} = 0.19$. Thus, $\beta_{CN} = -0.89\beta$ and $\beta_{NO} = -0.70\beta$. These approximations are quite crude, but it is unlikely that they have a major effect on the results of the calculation. The off diagonal overlap integrals were not neglected in order to reduce exaggeration of charge migration.[9a] The secular determinant is

$$\begin{vmatrix} -\epsilon & \beta_{CN} - S_{CN}\epsilon & 0 & 0 \\ \beta_{CN} - S_{CN}\epsilon & -\delta - \epsilon & \beta_{NO} - S_{NO}\epsilon & \beta_{NO} - S_{NO}\epsilon \\ 0 & \beta_{NO} - S_{NO}\epsilon & -\delta - \epsilon & 0 \\ 0 & \beta_{NO} - S_{NO}\epsilon & 0 & -\delta - \epsilon \end{vmatrix} = 0$$

where ϵ is the molecular orbital energy. By use of symmetry, the orbital, $\psi_2 = 2^{-1/2}(\varphi_O - \varphi_{O'})$, $\epsilon_2 = -\delta$, may be factored out and the determinant may be reduced to third order. ψ_2 proves to be the next to the lowest lying molecular orbital as indicated by its subscript.

Expansion of the third-order determinant gives the secular equation, $0.870x^3 + (1.942h - 0.959)x^2 + (h^2 - 0.427h - 1.772)x - 0.792h = 0$, where $x =$

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(7) For a more detailed theoretical discussion of these systems, see W. M. Schubert and W. A. Sweeney, *J. Am. Chem. Soc.*, **77**, 2297 (1955); O. H. Wheeler, *ibid.*, **78**, 3216 (1956).

(8) R. S. Mulliken, C. A. Rieke, D. Orloff, and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949); R. S. Mulliken, *J. Am. Chem. Soc.*, **72**, 4493 (1950).

ϵ/β and $h = \delta/\beta$. The roots, x_1, x_3, and x_4, of the equation were then determined for each value of h between 0 and 2.6 at 0.1 intervals. Since the ground state of the alkanenitronate was presumed to be $\psi_1{}^2$, $\psi_2{}^2$, and $\psi_3{}^2$, and the excited state $\psi_1{}^2$, $\psi_2{}^2$, $\psi_3{}^1$, $\psi_4{}^1$, the excitation energy is $\epsilon_4 - \epsilon_3$. The observed transition was 5.34 e.v. (~232 mμ). Thus, for each value of h, β was determined from the equation, $(x_4 - x_3)\beta = 5.34$. The plot of h *vs.* β in Figure 4 is then the combination of h and β values which give the observed excitation energy. The plot is parabolic indicating that for a range of β values, there are two h values which give the observed excitation energy.

The suggested values for the coulomb integral for oxygen tend to differ from that for carbon by about 2.0β, *i.e.*, $h = 2.0$.[9b] For the alkanenitronate, this coulomb integral for oxygen requires a β value of 2.7 e.v. to give the observed transition energy. This β value is in good agreement with those obtained by finding the β of best fit for a linear relationship between calculated and observed excitation energies.[9c,10]

The largest value for β (3.4 e.v.) obtained for the alkanenitronate in the range of h values investigated occurs at about $h = 1.1$. To obtain numerical values for the charge densities, the normalized, orthogonal molecular orbitals were calculated for $h = 1.1$ and $h = 2.0$.[11] The results are tabulated in Table III.[12]

Table III

Molecular orbitals	ϵ (β)
$h = 1.1$	
$\psi_1 = 1.327^{-1/2}(0.212\varphi_C + 0.734\varphi_N + 0.455\varphi_O + 0.455\varphi_{O'}$	−1.706
$\varphi_2 = 2^{-1/2}(\varphi_O - \varphi_{O'})$	−1.100
$\psi_3 = 0.938^{-1/2}(-0.525\varphi_C - 0.434\varphi_N + 0.517\varphi_O + 0.517\varphi_{O'})$	−0.609
$\psi_4 = 0.674^{-1/2}(0.705\varphi_C - 0.605\varphi_N + 0.206\varphi_O + 0.260\varphi_{O'})$	0.962
$h = 2.0$	
$\psi_1 = 1.298^{-1/2}(0.095\varphi_C + 0.724\varphi_N + 0.428\varphi_O + 0.428\varphi_{O'})$	−2.374
$\psi_2 = 2^{-1/2}(\varphi_O - \varphi_{O'})$	−2.000
$\psi_3 = 0.815^{-1/2}(-0.226\varphi_C - 0.632\varphi_N + 0.524\varphi_O + 0.524\varphi_{O'})$	−1.500
$\psi_4 = 0.767^{-1/2}(0.875\varphi_C - 0.442\varphi_N + 0.140\varphi_O + 0.140\varphi_{O'})$	0.512

In addition to the absorption band above 210 mμ considered here, there is very intense absorption below this wave length. This raises the question whether this end absorption shifts the maximum of the longer wave length band. Only the salt of 1-nitropropane has been investigated below 220 mμ (Figure 5). It appears that in this case the end absorption has little effect on the longer wave length maximum.

It is of interest that if the end absorption exhibits its maximum between 185 and 190 mμ (6.7–6.5 e.v.) it can be interpreted in terms of the calculated molecular orbital model as the $\psi_2 \rightarrow \psi_4$ transition. With this assumption, the energy of this transition differs from that of the $\psi_3 \rightarrow \psi_4$ transition (5.34 e.v.) by 1.2–1.4 e.v. The calculation for both h values gives a difference of about 0.5β for the two transitions. Using the suggested value of 2.7 e.v. for β, the calculated value is thus remarkably close. Furthermore, it appears that the shorter wave length transition is much more intense. This is consistent with the calculation since it suggests a similarly directed but greater charge migration for the $\psi_2 \rightarrow \psi_4$ transition.

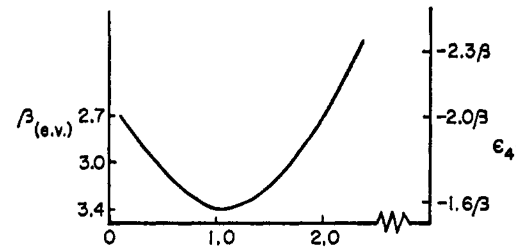

Figure 4.

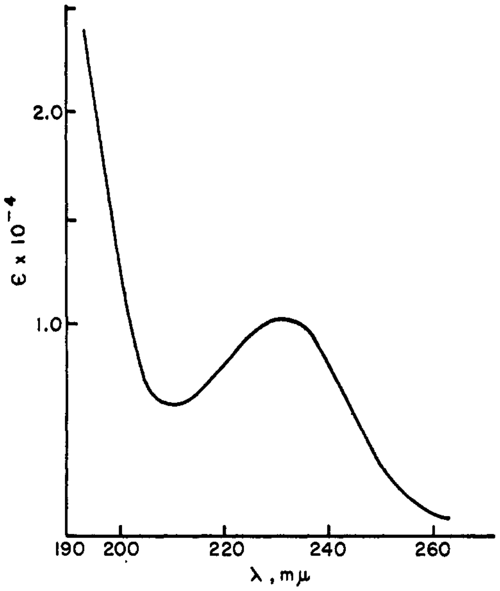

Figure 5.—Ultraviolet absorption spectrum of sodium 1-propanenitronate in water.

The calculated polarity for the carbonitronate is also in perfect qualitative agreement with that suggested by Pearson and Dillon.[13] On the basis of this assumed polarity the more rapid formation of the *aci* than of the nitro form of the nitroalkane on recombination of the carbonitronate with a proton results from the relatively much higher electron density on the oxygens of the carbonitronate than on its carbon. With this same polarity the order of ionization constants, 2-nitropropane > nitroethane > nitromethane, may be interpreted as the result of the low electron density on carbon which permits greater inductive stabilization of the carbonitronate as methyl is substituted for hydrogen.

The calculation indicates that in the range of h values from $h = 1.1$ to $h = 2.0$ and to some extent outside the range, the transition of an electron from the ψ_3 to the ψ_4 orbital causes a shift of negative charge toward carbon. Inspection of the carbon and nitrogen

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(9) A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961: (a) p. 118; (b) p. 135; (c) pp. 208–209.

(10) F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, Inc., New York, N. Y., 1963, pp. 288–289. It is undoubtedly fortuitous that this combination of h and β values happen to give an excitation energy so near that observed. For example, the β of best fit for linear polyenes and polyene aldehydes[9c] do not give the observed excitation energy of each substance in the correlation or even a constant fraction thereof.

(11) The interpretation of the results is based only on the *direction* and not the magnitude of charge migration and on the reduction in the C–N π-bond order indicated by the calculation. These conclusions would not be different for any h value between 1.1 and 2.0 and to some extent outside this range. An h of 2.0 is more in line with suggested values,[9b] but the calculated polarities for this value (Figure 3) indicate a large charge separation. Use of the ω technique would appear to have about the same effect as reducing h and hence polarities were also calculated for the lower value, $h = 1.1$ (Figure 2).

(12) Some aspects of the calculation related to the ground state can be compared with those of N. Jonathan [*J. Mol. Spectry.*, **7**, 105 (1961)].

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

coefficients of the ψ_3 and ψ_4 orbitals reveals a node between carbon and nitrogen in ψ_4 but not in ψ_3. Thus, there is a reduction in the C–N π-bond order on excitation of an electron from ψ_3 to ψ_4.

In summary, the variation of the observed spectral properties of the nitronate anions with their structures is readily interpreted in terms of the model suggested by the molecular orbital calculation. The calculated polarity of the carbonitronate is consistent with that proposed by Pearson and Dillon[13] to account for the pseudo acid and tautomeric properties of nitroalkanes. The bathochromic shift observed with cycloalkanenitronates (Table II) in changing from water to 50:50 dioxane–water is also readily interpretable in terms of the model.

To account for this solvent effect, it is suggested that water molecules are hydrogen bonded to the carbonitronate oxygens.[14] The effect of this bonding can be approximated by increasing the choice of the coulomb integral, δ, of the oxygen. In view of the fact that the orientation of solvent molecules does not change during excitation (Franck–Condon effect), this approach seems justified since the potential field for the π-electrons would be about the same in both the ground and excited states. Thus, if $\delta \geq 1.1$ is a reasonable parameter choice for nonhydrogen-bonded nitronates and hydrogen bonding increases the effective δ, it is seen that increasing δ increases the excitation energy, $\epsilon_4 - \epsilon_3$ (Figure 4). Thus, changing from water to 50:50 dioxane–water should reduce hydrogen bonding and cause the bathochromic shift.[15]

Experimental

Materials.—3,3-Dimethyl-1-nitrobutane was obtained from reaction of 1-bromo-3,3-dimethylbutane and potassium nitrite in DMSO. The nitroalkane was purified by regeneration from its salt and vacuum fractional distillation (b.p. 87° at 41 mm.). Its infrared spectrum showed no absorption bands for functional groups other than the nitro group.

1-Cyclobutynitromethane was obtained from reaction of cyclobutylmethyl tosylate and sodium nitrite in DMF (12% conversion b.p. 97° at 50 mm.). It was converted to cyclobutanecarboxaldehyde by permanganate oxidation of its salt.[17]

Anal. Calcd. for $C_5H_9NO_2$: C, 52.16; H, 7.88; N, 12.17. Found: C, 52.12; H, 8.04; N, 12.19.

1-Cyclopropylnitromethane was obtained by oxidation of cyclopropanecarboxaldoxime with peroxytrifluoroacetic acid in acetonitrile.[18] Its salt was converted by the Nef reaction to cyclopropanecarboxaldehyde.[19]

Anal. Calcd. for $C_5H_7NO_2$: C, 47.51; H, 6.93; N, 13.86. Found: C, 47.83; H, 6.89; N, 13.96.

Methods.—Each nitro compound (~0.1 g.) was stirred vigorously until solution was complete in a volume of standard aqueous sodium hydroxide (~0.1 *N*) calculated to give a 10:1 mole ratio of base to the nitro compound. The spectral samples were prepared by diluting aliquots of the alkaline solutions to approximately 10^{-4} *M* in nitro compound. The solutions were handled with minimum exposure to air and analyses were usually completed within 0.5 hr. after preparation of the solutions. The spectra were determined by single-point measurements in a Beckman DU spectrophotometer using 1-cm. silica cells. The shorter wave length measurements on sodium 1-propanenitronate (Figure 5) were determined on a Cary Model 14 spectrophotometer.

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[14] Evidence for hydrogen bonding in solutions of nitroalkanes has been given by P. J. Krueger [*Can. J. Chem.*, **42**, 288 (1964)]. Hydrogen bonding to nitronate anions may be expected to be even stronger.

[15] A similar conclusion is reached on the basis of considerations of orientation strain[16] in relation to the expected change (decrease) in the dipole moment of the anion accompanying excitation as estimated from the calculated polarities. This predicts a red shift in changing from water to the less polar dioxane–water solvent.

[16] H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 191.

[17] H. Shechter and F. T. Williams, Jr., *J. Org. Chem.*, **27**, 3699 (1962).

[18] An application of the general method of W. D. Emmons and A. S. Pagano, *J. Am. Chem. Soc.*, **77**, 4557 (1955).

[19] Isolated as the 2,4-dinitrophenylhydrazone, m.p. 185–186°, lit. m.p. 186–187.5°: C. L. Wilson, *ibid.*, **69**, 3002 (1947).

The Correlation of the Electronic Spectra, Acidities, and Polarographic Oxidation Half-Wave Potentials of 4-Substituted 2-Chlorophenols with Substituent Constants[1a]

HAROLD N. SIMPSON, C. KINNEY HANCOCK,[1b] AND EDWARD A. MEYERS

Department of Chemistry, Texas A & M University, College Station, Texas

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The electronic spectra, pK_A values, and polarographic oxidation half-wave potentials of a series of 4-substituted 2-chlorophenols (I) have been measured. Correlations of these data have been made and compared with correlations previously reported for a series of 4-substituted 2-nitrophenols (II) and a series of 5-substituted 2-nitrophenols (III). For all three of these series, there are excellent correlations between pK_A and σ, with the ρ value of -2.22 for I agreeing closely with that of -2.16 for II but being much more positive than that of -3.01 for III. As with II and III, there is a good correlation between ν_B and ν_A, but the relationship between $\Delta\nu$ and pK_A is unsatisfactory. Excellent correlations exist between $E_{1/2}$ and σ and between $E_{1/2}$ and pK_A. These and other relationships are discussed.

Recently, it has been shown that there is a quantitative relationship between the basic wave number shifts ($\Delta\nu = \nu_{\max}^{\mathrm{CHCl_3}} - \nu_{\max}^{\mathrm{NaOH}}$) of 2,4-dinitrophenylhydrazones[2,3] and the Hammett[4,5] and Taft[6] substituent constants for a wide range of substituents. A good relationship between the pK_A values and Hammett σ_p values has been established for a series of 4-substituted 2-nitrophenols.[7] A fair correlation between the

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[1] (a) Abstracted from the Ph.D. Dissertation of H. N. S., Texas A & M University, May 1964. (b) To whom inquiries should be addressed.

[2] L. A. Jones and C. K. Hancock, *J. Org. Chem.*, **25**, 226 (1960).

[3] L. E. Scoggins and C. K. Hancock, *ibid.*, **26**, 3490 (1961).

[4] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 188.

[5] H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

[6] R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 619.

[7] M. Rapoport, C. K. Hancock, and E. A. Meyers, *J. Am. Chem. Soc.*, **83**, 3489 (1961).