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SUBSTITUENT EFFECTS IN THE CHARGE-RESONANCE SPECTRA OF 1,1-DINITROALKANE ANIONS

Mortimer J. Kamlet and Donald J. Glover
Organic Chemistry Division, U. S. Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland, U. S. A.

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BALASUBRAMANIAN and Rao[1] have recently reported that frequencies of absorption maxima for the $n \rightarrow \pi^*$ transition of aliphatic nitro compounds are related linearly to Taft's σ^* if a treatment similar to that of Taft and Lewis[2] is applied to account for C-H and C-C hyperconjugation. We wish now to record a linear $\lambda_{max} - \sigma^*$ relationship for the primary bands in the charge-resonance spectra of 1,1-dinitroalkane anions, $R\text{-}C(NO_2)_2^-$, a series in which the non-conjugating substituent R has a pronounced inductive influence on the position of the maximum.

Spectra were determined using the potassium salts in 3-5 x 10^{-5} molar concentrations in dilute aqueous alkali and previously described precautions were taken in carrying out all measurements[3]. Absorption maxima for a number of such compounds for which σ^* of R was available or could be deduced are listed in Table I. Extinction coefficients were in the order of 15-20,000 and all spectra showed minima with ε = 1,000 or less in the

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[1] A. Balasubramanian and C. N. R. Rao, Chem. and Ind. 1025 (1960).

[2] R. W. Taft, Jr. and I. C. Lewis, Tetrahedron 5, 210 (1959).

[3] M. J. Kamlet and L. A. Kaplan, J. Org. Chem. 22, 576 (1957).

280-300 mμ region, so that complications due to band overlap had negligible influence on the positions of λ_{max}.

TABLE I

No.	$R-C(NO_2)_2^-$, R =	σ^{*}[h]	λ_{max}, mμ	Ref.
XXXV	$t-C_4H_9CH_2$	-0.165	384	a
XXXIV	$i-C_4H_9$	-0.130	384	a
V	$n-C_4H_9$	-0.125	382 (384)	b (a)
III	C_2H_5	-0.100	382 (383)	b (a)
II	CH_3	0.000	381.5 (381)	b (c)
XI	$CH_3COCH_2CH_2$	+0.214[d]	379	b
VII	$(CH_3)_2NCH_2$	+0.22[e]	369.5	b
X	$CH_3OOCCH_2CH_2$	+0.255[f]	379	b
XXIX	$NO_2CH_2CH_2$	+0.50	374	b
XXXVI	$CH_3CH_2OCH_2$	+0.52[g]	365	b
VIII	$HOCH_2$	+0.555	365	b
IX	C_6H_5	+0.600	373	b
VI	$N{\equiv}CCH_2$	+1.300	362.5	b
XXIII	$(CH_3)_3\overset{+}{N}CH_2$	+1.90	352	c

[a] Private communication, Dr. H. Shechter, Ohio State University.

[b] Spectra determined in present investigation.

[c] L. Zeldin and H. Shechter, J. Amer. Chem. Soc. 79, 4708 (1957).

[d] Estimated by dividing value for CH_3COCH_2 by 2.8.

[e] R. W. Taft and I. C. Lewis, J. Amer. Chem. Soc. 80, 2436 (1958).

[f] Estimated by dividing the value for C_2H_5OOC by $(2.8)^2$.

[g] Estimated to be same as value for CH_3OCH_2.

[h] R. W. Taft, Jr. in M. S. Newman, Steric Effects in Organic Chemistry. John Wiley and Sons, New York, 1956, Chapter 13.

Of the fourteen dinitroalkane anions, the $\lambda_{max} - \sigma^*$ plot (Figure 1) shows eleven conforming with the expression,

$$\lambda_{max} = (381.6 - 15.25\ \sigma^*)\ m\mu, \qquad (1)$$

the average deviation being less than 0.5 mμ. Compounds VII, VIII and XXXVI, 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 <u>beta</u> to the charged carbon. If the expression is modified as follows,

$$\lambda_{max} = (381.6 - 15.25\ \sigma^* - 8.5\ \gamma)\ m\mu, \qquad (2)$$

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

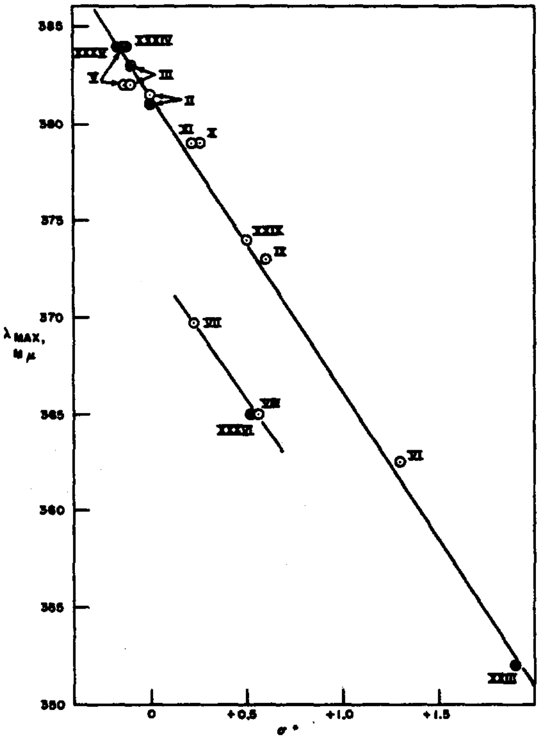

FIG. I. λ MAX RELATED TO σ^*. ⊙ - PRESENT INVESTIGATION. ● - DATA OF SHECHTER

It is noteworthy that λ_{max} shifts hypsochromically with increasing ability of the substituent to delocalize the negative charge by inductive withdrawal of the C-R electron pair in the direction of R. This is in marked contrast with the effect of conjugating electron-withdrawing substituents which generally shift charge-resonance maxima of carbanions bathochromically by providing additional "seats for the resonating charge"[4].

The preparation of the compounds listed in Table I and a more detailed account of the spectra of 1,1-dinitroalkane anions will be presented in future papers. The authors are grateful to Dr. H. Shechter for making available unpublished information and to Drs. L. A. Kaplan, J. C. Dacons and D. V. Sickman for helpful discussions.

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[4] E. A. Braude in E. A. Braude and F. C. Nachod, Determination of Organic Structures by Physical Methods. Academic Press, New York, 1955, p. 158.