Tetrahedron, 1959. Vol. 6, pp. 1 to 9. Pergamon Press Ltd. Printed in Northern Ireland

A STUDY OF THE HYDROGEN BONDS BETWEEN THE NITRO-GROUP AND THE HYDROXYL OR AMINO-GROUPS IN SUBSTITUTED NITROPARAFFINS

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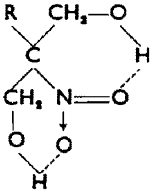
Abstract—The ultra-violet absorption spectra of many nitro paraffin derivatives containing hydroxyl and or amino groups, do not show a maximum (260–270 mμ) typical of the nitro group. This is attributed to the formation of six-membered chelate rings by internal hydrogen bonds between the nitro and hydroxyl or amino groups. *Two* hydroxyl groups or *one* secondary amino group are necessary to transform the normal maximum of the nitro group into a bend. This is considered as new evidence for the mainly electrostatic nature of the hydrogen bond. Hydrogen bonds between nitro and hydroxyl or amino groups also produce a bathochromic effect; the corresponding maxima or shoulders being shifted towards longer waves (270–285 mμ).

THE effect of the hydrogen bond on electronic spectra has recently been reviewed.[1] Morton and Stubbs,[2] proved in the case of hydroxybenzaldehydes that both inter- and intra-molecular bonds, and association between solute and solvent can produce a shift of the benzenoid ultra-violet absorption bands towards longer wavelengths. The degree of shift for different isomers depends on the strength of the bonds. Burawoy *et al.*[3] have confirmed this by comparing electronic spectra of substituted phenol and anisole. The abnormal ultra-violet absorption spectra[4] of nitro paraffin derivatives containing hydroxyl and or amino groups are considered to be due to the formation of six-membered chelate rings[4,5] by internal hydrogen bonds between the nitro group and the hydroxyl or amino group. Two hydroxyl groups or one amino group forming the chelate rings (formulae A and B) are required to transform the normal maximum of the nitro group into a shoulder; the presence of a single hydroxyl group and consequent hydrogen bonding has a bathochromic effect, but does not appreciably alter the shape of the ultra-violet spectra. The stronger electron repelling properties of the amino as compared with the hydroxyl group, together with the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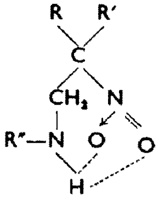
B

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[1] *IUPAC Symposium on Hydrogen Bond*, Ljubljana (1957). W. F. Forbes and J. F. Templeton, *Chem. & Ind.* **77**, (1957).

[2] R. A. Morton and A. L. Stubbs, *J. Chem. Soc.* 1347 (1940).

[3] A. Burawoy and J. T. Chamberlain, *J. Chem. Soc.* 2310 (1952). A. Burawoy, M. Cais, J. T. Chamberlain, F. Liversedge and A. R. Thompson, *Ibid.* 3721, 3727 (1955).

[4] T. Urbański, *Bull. Acad. Pol. Sci.* Cl. III, **1**, 239 (1953).

[5] T. Urbański and D. Ciecierska, *Roczn. Chem.* **29**, 11 (1955); T. Urbański, *Bull Acad. Pol. Sci.* Cl.III **2**, 393 (1954); *Roczn. Chem.* **29**, 375 (1955); T. Urbański, *IUPAC Symposium on Hydrogen Bond*, Ljubljana (1957).

electron attracting properties of the nitro group are considered evidence supporting the view that the hydrogen bond is mainly electrostatic.

All compounds investigated produce a strong absorption band near 200 mμ. This may be produced by single bonded atoms or groups with single bonds (auxochroms), such as —O—, $>$N— and —C—C—.[6] The existence of hydrogen bonds between hydroxyl or amino groups and a nitro group has been confirmed by infra-red absorption spectra.[7]

EXPERIMENTAL

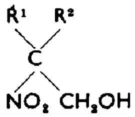
In the present paper, previously published and unpublished results are given. A quartz Beckman spectrophotometer (model DU) with hydrogen lamp and 1–4 mμ beam width was used. Measurements were made every 5 mμ on aqueous or ethyl alcohol solutions of the compounds.

The names or structural formulae of all compounds are:

Nitroparaffins

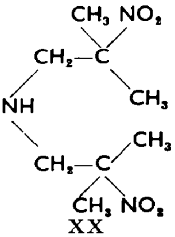
I Nitromethane
II Nitroethane
III 1-Nitropropane
IV 2-Nitropropane
V 1-Nitro-*n*-butane
VI 1-Nitro*iso*butane
VII 1-Nitro-*n*-pentane
VIII 1-Nitro-*n*-hexane

Nitroalcohols



IX $R^1 = R^2 = H$
X $R^1 = R^2 = CH_2OH$
XI $R^1 = CH_3,\ R^2 = H$
XII $R^1 = CH_3,\ R^2 = CH_2OH$
XIII $R^1 = C_2H_5,\ R^2 = H$
XIV $R^1 = C_2H_5,\ R^2 = CH_2OH$
XV $R^1 = R^2 = CH_3$
XVI $R^1 = C_3H_7,\ R^2 = CH_2OH$
XVII $R^1 =$ *iso*-$C_3H_7,\ R^2 = CH_2OH$
XVIII $R^1 = C_4H_9,\ R^2 = CH_2OH$
XIX $R^1 = C_5H_{11},\ R^2 = CH_2OH$

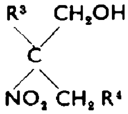
Aminonitro compound



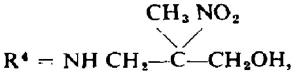
XX

XXI hydrochloride of XX

Aminonitroalcohols

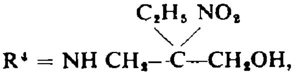


XXII $R^3 = C_2H_5,\ R^4 = NH_2$, hydrochloride
XXIII $R^3 = C_3H_7,\ R^4 = NH_2$, hydrochloride
XXIV $R^3 = C_3H_7,\ R^4 = NHCH_3$, hydrochloride
XXV $R^3 = C_3H_7,\ R^4 = NHC_2H_5$, hydrochloride
XXVI $R^3 =$ *iso*-$C_3H_7,\ R^4 = NH_2$, hydrochloride
XXVII $R^3 = C_4H_9,\ R^4 = NH_2$, hydrochloride
XXVIII $R^3 = C_4H_9,\ R^4 = NHCH_3$, hydrochloride
XXIX $R^3 = CH_3$,



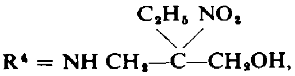
$R^4 = NH\ CH_2—\overset{CH_3\ NO_2}{C}—CH_2OH$, hydrochloride

XXX $R^3 = C_2H_5$,



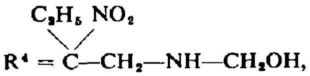
$R^4 = NH\ CH_2—\overset{C_2H_5\ NO_2}{C}—CH_2OH$,

XXXI $R^3 = C_2H_5$,



$R^4 = NH\ CH_2—\overset{C_2H_5\ NO_2}{C}—CH_2OH$, hydrochloride

XXXII $R^3 = C_2H_5$,



$R^4 = \overset{C_2H_5\ NO_2}{C}—CH_2—NH—CH_2OH$, hydrochloride

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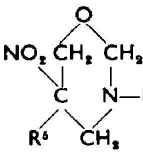
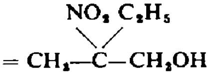
[6] E. A. Braude, *Ann. Rep. Progr. Chem.* **42**, 105 (1945).

[7] T. Urbański, *Bull. Acad. Polon. Sci.* Cl. III. **4**, 87, 381 (1956); *Roczn. Chem.* **31**, 37 (1957).

1:3-*Tetrahydro-oxazine derivatives*

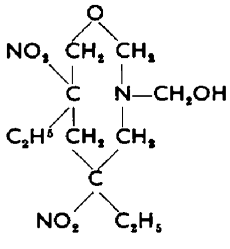


XXXIII $R^5 = C_2H_5$, $R^6 = H$, hydrochloride
XXXIV $R^5 = C_2H_5$, $R^6 = CH_3$, hydrochloride
XXXV $R^5 = C_2H_5$, $R^6 = (CH_3)_2\ I^{\ominus}$



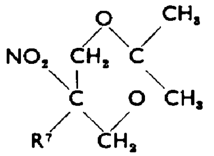
XXXVI $R^5 = C_2H_5$ $R^6 = CH_2{-}\overset{NO_2\ C_2H_5}{C}{-}CH_2OH$
XXXVII $R^5 = C_3H_7$, $R^6 = H$, hydrochloride
XXXVIII $R^5 = C_3H_7$, $R^6 = CH_3$, hydrochloride
XXXIX $R^5 = C_3H_7$, $R^6 = C_2H_5$, hydrochloride
XL $R^5 =$ *iso*-C_3H_7, $R^6 = H$, hydrochloride
XLI $R^5 =$ *iso*-C_3H_7, $R^6 = CH_3$, hydrochloride
XLII $R^5 =$ *iso*-C_3H_7, $R^6 = C_2H_5$, hydrochloride
XLIII $R^5 = C^4H_9$, $R^6 = H$, hydrochloride
XLIV $R^5 = C_4H_9$, $R^6 = CH_3$, hydrochloride
XLV $R^5 = C_4H_9$, $R^6 = C_2H_5$, hydrochloride

1-*Oxa*-3-*aza*-*cyclooctane derivative*

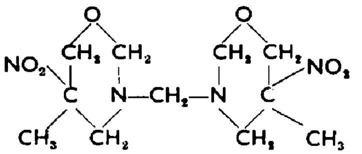


XLVII

1:3-*Dioxane derivatives*



XLVIII $R^7 = CH_3$
XLIX $R^7 = CH_2OH$



XLVI

All compounds, from (IX) onwards have been prepared according to the literature; compounds (IX–XIX) according to Vanderbildt and Hass[8] and Urbański and Chylińska.[9]

All other compounds were prepared according to methods described by other workers and the present author.[10]

In addition to the compounds containing a nitro group, the absorption spectra of two derivatives of 1:3-tetrahydro-oxazine without a nitro group, have also been

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[8] B. M. Vanderbildt and H. B. Hass, *Industr. Engng. Chem.* **32**, 34 (1940).

[9] T. Urbański and B. Chylińska, *Roczn. Chem.* **31**, 695 (1957).

[10] E. L. Hirst, J. K. N. Jones, S. Minahan, F. W. Ochyński, A. T. Thomas and T. Urbański, *J. Chem. Soc.* 924 (1947); J. K. N. Jones and T. Urbański, *Ibid.* 1766 (1949); T. Urbański and S. Malinowski, *Roczn. Chem.* **25**, 183 (1951); T. Urbański and E. Lipska, *Ibid.* **26**, 182 (1952); T. Urbański and H. Piotrowska, *Bull. Acad. Pol. Sci.* Cl. III, **3**, 389 (1955); *Roczn Chem.* **29**, 379 (1955); **31**, 553 (1957); T. Urbański and J. Kolesińska, *Ibid.* **29**, 392 (1955); T. Urbański and D. Gürne, *Bull. Acad. Pol. Sci.* Cl. III. **3**, 175 (1955); **4**, 221 (1956); *Roczn. Chem.* **31**, 855, 869 (1957); T. Urbański, H. Dabrowska, B. Lesiowska, H. Piotrowska, *Ibid.* **31**, 687 (1957).

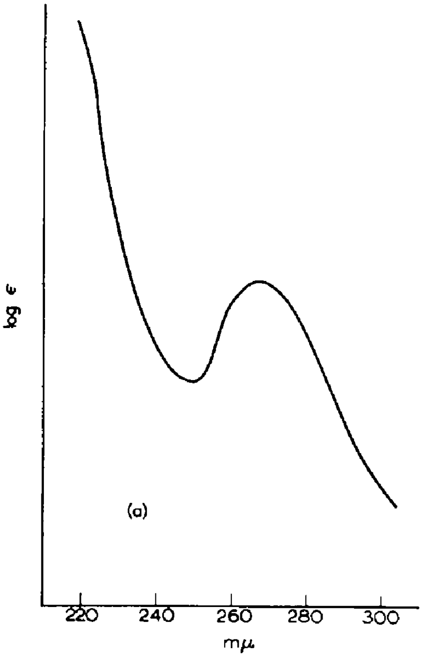


FIG. 1. Curve (a)—with a strong maximum.

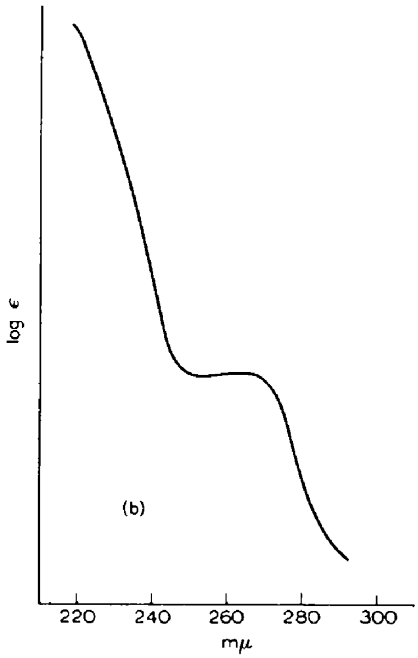


FIG. 2. Curve (b)—with a very weak maximum, or a very strong shoulder.

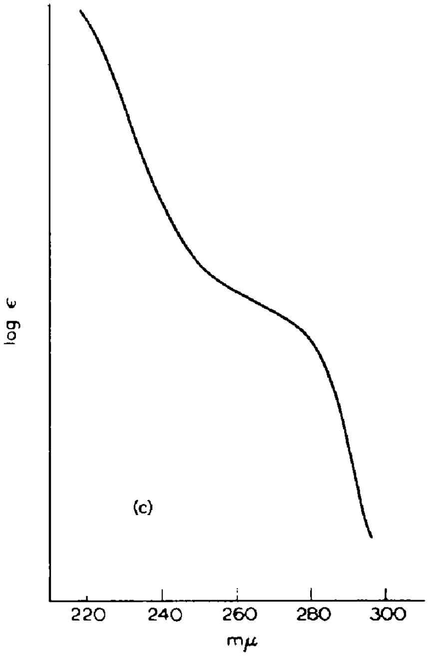


FIG. 3. Curve (c)—with a clear bend.

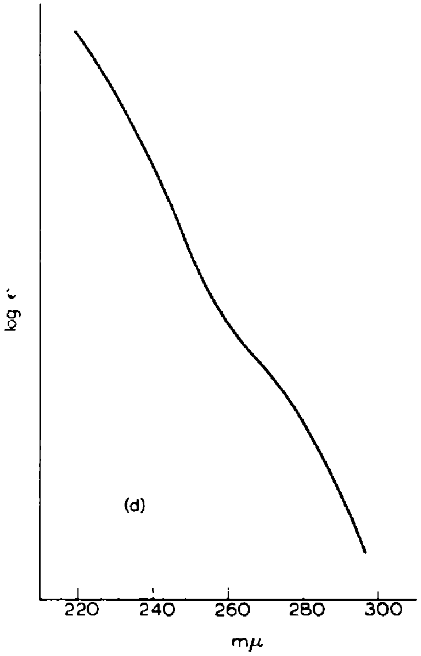
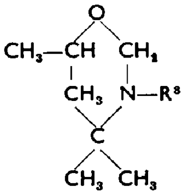


FIG. 4. Curve (d)—with a very weak bend.

examined. They are compounds (L) and (LI), which have been



L R^8 = H, hydrochloride
LI R^8 = CH_3, hydrochloride

prepared according to Kohn.[11,12]

All absorption curves can be classified in four types (Fig. 1–4)

All numerical results are tabulated (Tables 1 and 2)

TABLE 1

Substance	Solvent	Minimum			Maximum			Δε	Shape of the curve
		wave-length (mμ)	log ε	ε	wave-length (mμ)	log ε	ε		
I	Alcohol	250	1·50	31·7	260	1·59	39·1	7·4	A
II	Alcohol	250	1·54	34·3	260	1·63	42·3	8·0	A
III	Alcohol	250	1·07	11·8	270	1·59	39·3	27·5	A
IV	Alcohol	250	1·58	37·7	260	1·66	45·7	8·0	A
V	Alcohol	247	1·17	15·0	272	1·40	25·4	10·4	A
VI	Alcohol	245	2·05	112·5	255	2·09	121·7	9·2	A
VII	Alcohol	250	1·40	24·9	270	1·51	32·2	7·3	A
VIII	Alcohol	248	1·48	30·2	261	1·55	35·7	5·5	A
IX	Alcohol	258	1·43	27·0	270	1·45	28·1	1·1	A
X	Alcohol	265	1·53	33·6	275	1·53	33·6	0·0	B
	Water		a bend		c282	1·60	40·1	—	C
XI	Alcohol	250	1·24	17·4	275	1·49	31·1	13·7	A
XII	Alcohol	262	1·42	26·4	275	1·52	32·9	6·5	A
	Water	268	1·54	34·7	275	1·54	34·7	0·0	B
XIII	Alcohol	251	1·28	18·9	279	1·47	29·4	10·5	A
XIV	Alcohol		a bend		c280	1·61	40·4	—	C
	Water		a bend		c285	1·46	29·3	—	C
XV	Alcohol	252	1·23	16·9	278	1·49	31·0	14.1	A
	Water	255	1·28	17·8	280	1·47	29·8	12.0	A
XVI	Water		a bend		c280	1·57	37·2	—	C
XVII	Water		a bend		c275	1·70	50·7	—	C
XVIII	Water		a weak bend		c280	1·59	38·9	—	D
XIX	Water		a bend		c275	1·62	41·5	—	C

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[11] M. Kohn, *Monatshefte* **25**, 135, 817, 830, 850 (1904);

[12] T. Urbański and B. Gac-Chylińska, *Roczn. Chem.* **30**, 185 (1956).

TABLE 2

Substance	Solvent	Minimum			Maximum			Δε	Shape of the curve
		wave-length (mμ)	log ε	ε	wave-length (mμ)	log ε	ε		
XX	Alcohol	250	2·87	741	256	2·90	794	53	A
XXI	Water		a bend c		280	1·85	70·7	—	C
XXII	Water		a bend		c280	1·64	43·9	—	C
XXIII	Water		a weak bend		c275	1·81	65·3	—	D
XXIV	Water		a weak bend		c280	1·55	35·8	—	D
XXV	Water		a bend		c285	1·52	33·2	—	C
XXVI	Water		a bend		c275	1·72	52·8	—	C
XXVII	Water		a bend		c272	1·62	41·8	—	C
XXVIII	Water		a weak bend		c280	1·66	45·7	—	D
XXIX	Water		a bend		c250	2·79	623	—	C
XXX	Water		a bend		c270	2·73	540	—	C
XXXI	Alcohol		a bend		c265	2·52	331	—	C
XXXII	Water		a bend		c260	2·48	302	—	C
XXXIII	Water	260	1·78	60·4	272	1·81	64·3	3·9	A
XXXIV	Water	255	1·57	37·3	270	1·61	40·3	3·0	A
XXXV	Water	272	1·60	39·8	278	1·60	39·8	0·0	B
XXXVI	Alcohol	248	2·64	437	260	2·68	477	40	A
XXXVII	Water	256	1·73	53·7	275	1·82	66·1	12·4	A
XXXVIII	Water	255	1·52	33·0	273	1·58	38·2	5·2	A
XXXIX	Water	245	1·98	95·9	260	1·98	95·9	0·0	B
XL	Water	257	1·56	36·5	275	1·61	40·9	4·4	A
XLI	Water	252	1·48	30·2	277	1·65	44·4	14·2	A
XLII	Water	255	1·44	27·9	280	1·64	43·8	16·1	A
XLIII	Water	255	1·49	30·9	275	1·55	35·3	4·4	A
XLIV	Water	255	1·53	34·1	275	1·60	40·2	6·1	A
XLV	Water	262	1·59	39·0	270	1·60	39·8	0·8	A-B
XLVI	Alcohol	250	2·77	593	262	2·80	631	38	A
XLVII	Alcohol	250	2·63	431	260	2·67	470	39	A
XLVIII	Alcohol	260	1·29	19·4	278	1·40	24·9	5·5	A
XLIX	Alcohol	265	1·18	15·1	284	1·34	21·9	6·8	A
L	Water		a very weak bend		c240	0·8	6·3	—	D
LI	Water		a very weak bend		c230	1·4	25·1	—	D

DISCUSSION

New results described in this paper confirm fully previous observations and all former statements have been confirmed. In addition, a few more conclusions may be drawn.

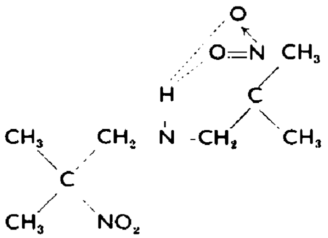
Dinitrocompounds: (XX, XXIX–XXXII, XXXVI, XLVI and XLVII) are composed of two molecules of nitro paraffins; they are distinguished by their high extinction coefficients.

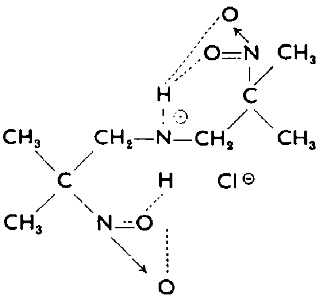
In (XX) one nitro group may be bonded by a bifurcated hydrogen bond and the second "free" (XXa), or both nitro groups may be partially bonded (XXb).

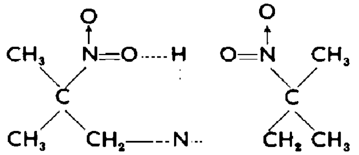
Compound (XX), shows a relatively strong extinction (c.800) at the maximum characteristic of the nitro group, the shape of the absorption curve (a) agreeing with the structure (XXa). The hydrochloride (XXI) shows a much lower extinction (of the order of 70) at the bend [curve (c)] and no maximum of the nitro group (XXIa).

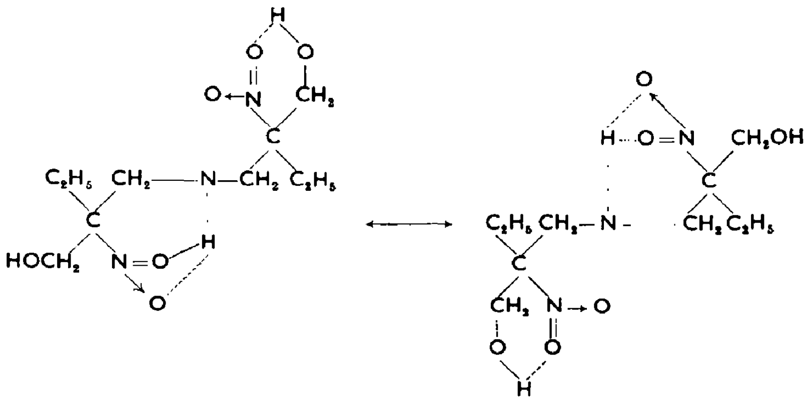
It is suggested that (XXa) with two nitro groups, one of which is "free", is responsible for the high extinction. In contrast, fully bonded two nitro groups (XXIa) give a relatively low extinction, although it is higher than in the case of the compounds with one nitro group.

The compounds with two nitro groups (XXIX, XXX, XXXI and XXXII) in form of hydrochlorides with sufficient hydrogen atoms to transform the maximum of the nitro group, show a relatively high extinction of the order of 300 to 600 (lower than XX). Mesomeric structures, (e.g. XXXa and XXXb), could be suggested for this type of

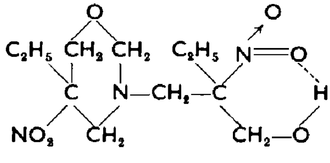

XXa


XXIa


XXb


XXXa XXXb

compound. Compounds with two unbonded or partially bonded nitro groups (XXXVI, XLVI, XLVII—a typical structure being XXXVIa) also give a high extinction.



XXXVIa

Aminonitroalcohols with relatively long chain molecules of the type (XXIX–XXXII) show a higher extinction than aminonitroalcohols with one nitro group (XXII–XXVIII).

Ring compounds with: (i) a long side chain (XXXVI); (ii) two 1:3-oxazine rings, each containing a nitro group (XLVI); (iii) a larger (eight member) ring with two nitro groups (XLVII), all give a higher extinction coefficient than simpler 1:3-oxazine derivatives (XXXIII, XXXIV, XXXVII–XLV).

1:3-*Tetrahydro-oxazine compounds* with a 5-nitro-1:3-tetrahydro-oxazine ring give a clear maximum characteristic of a nitro group. No hydrogen bond is possible between the nitro group and N-hydrogen in compounds (XXXIII, XXXVII, XL, XLIII), the distance between oxygen atoms and N-hydrogen being larger than 3 Å.

The N-ethyl groups (XXXIX and XLV) produce a steric influence upon the nitro group shown by weakening of the absorption maximum, curve (b). The same applies to the quaternary iodide (XXXV) where two N-methyl groups and the iodine ion are present. In contrast, it is difficult to explain the lack of the effect of N-ethyl in (XLII).

Compounds with a 1:3-oxazine ring and no nitro group (XL and XLI) show a strong maximum in the proximity of 200 mμ, which seems to be characteristic of all substances described in the present paper. The lack of a chromophore in these molecules may be responsible for the very small extinction coefficient in the absorption curves of (XL) and (XLI) at 240 and 230 mμ respectively.

The absorption spectra of 1-nitrobutane (V) and 1-nitro*iso*butane (VI) and also those of their respective diols (XVI and XVII), conform to the general rule that branched alkyls produce a higher extinction coefficient than straight chain ones.[13] This rule, however, does not apply to some 1:3-oxazine derivatives, (XXXVII and XXXIX) from 1-nitrobutane possessing a slightly higher coefficient than the corresponding derivatives (XL and XLII) of 1-nitro*iso*butane.

Bathochromic effect

When internal hydrogen bonds are present the maximum produced by the nitro group or the bend corresponding to this maximum is shifted towards longer wavelengths.

This bathochromic effect can be observed when comparing maxima in nitro paraffins with maxima or bends in the corresponding nitro alcohols. Thus, when nitromethane (I, max 260 mμ); was converted to a monohydroxylic alcohol (IX) the maximum was shifted to 270 mμ; and when three alcoholic groups were introduced, (the triol X) the maximum was transformed into a bend at c. 275 mμ (all in alcoholic

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[13] A. E. Fehnel and M. Cormack, *J. Amer. Chem. Soc.* 71, 84 (1949).

solution). In the case of nitroethane (II) the maximum, 260 mμ was shifted to 275 mμ in the monol (XI), and the same wavelength was found for the bend in the case of the diol (XII).

A comparison of nitro paraffins and nitro alcohols with the same number of carbon atoms leads to the same conclusion. Alcohol (IX) has the maximum at 270 mμ, i.e. at a higher wavelength than nitroethane.

A similar shifting was observed in the case of 1-nitropropane (III, 270 mμ) and the corresponding monol (XIII, max 279 mμ) and diol (XIV, bend at c. 280 mμ). 2-Nitropropane (IV) has the maximum at 260 mμ and the alcohol (XV) gives a maximum at 278 mμ. 2-Nitropropane should also be compared with 2-nitropropane-1-ol (XI) which shows an absorption band at a longer wavelength (275 mμ). It should be pointed out, that although one hydroxyl group is not sufficient to transform a maximum into a bend, it can produce a shifting of the maximum of the nitro group. All higher nitro paraffins (V–VII) show the same type of shifting from 272, 255, 270, 261 mμ to 280, 275, 280, 275 mμ respectively after being transformed into the corresponding diols (XVI–XIX).

The same wavelengths (272–285 mμ) of the bends corresponding to the bonded nitro group was also found in amino-nitro alcohols derived from nitro paraffins.

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