[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

The Infrared Spectra of Nitro and Other Oxidized Nitrogen Compounds

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Study of the infrared spectra of nitro compounds has shown that the positions and intensities of the NO_2 asymmetrical and symmetrical stretching bands can be correlated with the electron-releasing ability of the structure attached to the nitro group, the presence of negative groups on the carbon holding the nitro group and conjugation of the nitro group. These correlations can be related directly to the electronic structure of the nitro group. Various specific interactions also can be recognized in the spectra of compounds having nitro groups attached to benzenoid, olefinic or methylene groups, or to carbons which also carry other nitro or methyl groups. As a result of these various correlations, it is possible to distinguish among, and reliably identify, many types of structures containing nitro groups. In addition to the nitro compounds, nitrate and nitrite esters, nitroso dimers, azoxy compounds, furoxanes, oximes, oxime ethers and hydroxylamines also can be readily identified from their infrared spectra.

Studies of aliphatic nitration processes and the products obtained thereby revealed an acute need for new methods of identifying organic compounds containing oxidized nitrogen, particularly nitro compounds. In hopes of satisfying this need, a study of the infrared spectroscopy of such compounds was undertaken. This study had three objectives: first, to find out how well different classes of oxidized nitrogen compounds could be distinguished from one another; second, to find out how effectively a distinction between different types of nitro compounds could be made; and third, to gain a sufficient understanding of the basic factors involved in the latter distinctions so that the infrared correlations could be used with confidence in structural determinations.

Experimental

The spectra of about 150 compounds were determined, using a Perkin-Elmer model 21 infrared spectrophotometer, or, in some cases, a Baird associates model B instrument. In some cases, water vapor spectra were run on the same spectrophotometer tracing immediately after running the sample in order to provide calibration in the 6.0–7.5 μ region; such calibrated spectral data were highly reproducible, and presumably accurate to ±0.01 μ. Intercorrelation of the other results indicated that the spectra run as routine samples on the Perkin-Elmer instrument were reliable to ±0.03 μ, while single value determinations on the Baird instrument were reliable to ±0.05 μ. Where the spectra were determined to ±0.01 μ, the molar extinction coefficients and half intensity band widths of the principal spectral bands were also estimated. However, because of the number of arbitrary assumptions which are involved in making such estimates on spectral bands which are not entirely free from overlapping with other bands, these results will not be reported in detail. The spectral data obtained are reported in Table I. Such data represent averages of generally one to four determinations on each compound. In order to avoid multiple listing of polyfunctional compounds, and to facilitate location of specific compounds from the table, the compounds studied have been listed in Table I by their empirical formulas, listing dimers and polymers under the parent monomer.

Results

Nitroalkanes.—Of pre-eminent importance in the infrared spectroscopic study of nitro compounds and nitrate esters are the bands resulting from the fundamental vibrations of the XNO_2 group. These vibrations are shown in Fig. 1. A theoretical study of the spectra of nitromethane showed that in this simplest nitroalkane, the positions of the CNO_2 group fundamentals are

NO_2 asym. str.	6.37 μ	NO_2 bend.	15.24 μ
NO_2 sym. str.	7.25	Out of plane	16.24
C–N str.	10.90	CNO bend.	20.75

Similar bands were seen in other simple nitroalkanes, and empirical assignments of the CNO_2 fundamentals made.[1] These and earlier[2] empirical assignments indicated that the nitro alkanes are characterized by NO_2 stretching bands near 6.4 and 7.3 μ, and by C–N stretching near 11.6 μ.

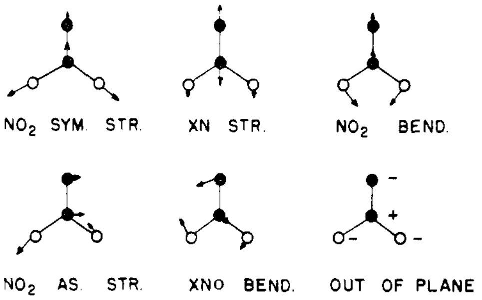

Fig. 1.—Fundamental vibrations of XNO_2 structures.

In accordance with the previous results, our studies of a variety of types of nitroalkanes showed that the most characteristic features of the infrared spectra are the very strong NO_2 asymmetrical stretching band at 6.2–6.5 μ (*E ca.* 500) and the NO_2 symmetrical stretching band at 7.2–7.6 μ (*E ca.* 100). The positions of these bands in a variety of types of compounds containing the $-NO_2$ group are shown in Table II.

We were less successful, however, in finding the C–N stretching band indicated by the previous workers. Even in closely related compounds, we could discover no consistent behavior in the 11–12 μ region which would permit empirical assignments for the C–N stretching mode to be made. Moreover, a determination of the intensity of the known C–N stretching band in nitromethane showed that it was rather weak ($E = 13$ in chloroform solution). A band of this intensity should not be readily identified in the structural vibration region of a more complex molecule. We concluded, therefore, that arbitrary empirical assignments of the C–N stretching mode to prominent bands in the 11–12 μ region are not justifiable. The other CNO_2 group fundamentals lie beyond the 2–15 μ range covered by our instrument.

Splitting of the NO_2 asymmetrical and symmetrical stretching bands due to vibrational interactions

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[1] D. C. Smith, C. Y. Pan and J. R. Nielsen, *J. Chem. Phys.*, **18**, 706 (1950).

[2] J. P. Mathieu and D. Massignon, *Compt. rend.*, **212**, 1084 (1941).

TABLE I

INFRARED BANDS IN OXIDIZED NITROGEN COMPOUNDS

Empirical formula	Name	Type[a]	State[b]	Accuracy[c]	Bands of group								Miscellaneous
					NO_2	NO_2	CH_2	ONO_2	ONO_2	ONO_2	ONO_2	ONO_2	
CCl_3NO_2	Chloropicrin	3′′′	cl	01	6.21	7.62	..	..	..	...	...	...	
CH_3NO_2	Nitromethane	1	cl	01	6.38	7.26	7.03	..	..	...	...	...	
CH_3NO_3	Methyl nitrate	N	l	05	..	..	..	6.12	7.78	11.63	13.16	...	
$C_2ClH_4NO_2$	1-Chloro-1-nitroethane	2′	l	03	6.37	7.42	..	..	..	...	...	...	
$C_2Cl_2H_3NO_2$	1,1-Dichloro-1-nitroethane	3″	l	03	6.30	7.55	..	..	..	...	...	...	
$C_2H_3KN_2O_4$	1,1-Dinitroethane, K salt		s	03	8.05	8.69	..	..	..	...	...	...	
$C_2H_3NO_2$	Nitroethylene	0 I	l	03	6.55	7.39	..	..	..	...	...	...	6.09, 10.36, 10.64[d,m]
$C_2H_4N_2O_4$	1,1-Dinitroethane[e]	2′	l	03	6.30	7.48	..	..	..	...	...	...	...
$C_2H_5NO_2$	Nitroethane	1	cl	01	6.42	7.31	6.94	..	..	...	...	...	7.17[p]
$C_2H_5NO_3$	2-Nitroethanol	1	l	03	6.43	7.30	7.05	..	..	...	...	...	...
$C_3ClH_6NO_2$	2-Chloro-2-nitropropane	3′	cl	01	6.39	7.45	..	..	..	...	...	...	[n]
$C_3H_5NO_2$	1-Nitro-1-propene	0 II	l	03	6.58	7.42	..	..	..	...	...	...	[f]
$C_3H_5NO_2$	1-Nitro-2-propene	1 I	l	03	6.41	7.28	7.04	..	..	...	...	...	6.07, 10.09, 10.57[d,m]
$C_3H_6N_2O_4$	1,1-Dinitropropane[e]	2′	l	03	6.32	7.52	..	..	..	...	...	...	...
$C_3H_6N_2O_4$	2,2-Dinitropropane	3′	cl	01	6.36	7.52	..	..	..	...	...	...	[n]
$C_3H_7NO_2$	2-Nitropropane	2	cl	01	6.44	7.35	..	..	..	...	...	...	[n]
$C_4Br_2H_7NO_2$	1,2-Dibromo-1-nitrobutane	2’	cl	01	6.34	7.42	..	..	..	...	...	...	...
$C_4ClH_6NO_2$	1-Chloro-1-nitrobutene	O′ IV	cl	01	6.47	7.51	..	..	..	...	...	...	6.12, 12.69[d]
$C_4ClH_8NO_2$	2-Chloro-1-nitrobutane[g]	1	l	03	6.41	7.25	7.05	..	..	...	...	...	...
$C_4Cl_2H_7NO_2$	1,2-Dichloro-1-nitrobutane[g]	2′	cl	01	6.33	7.40	..	..	..	...	...	...	...
$C_4Cl_3H_6NO_2$	1,1,2-Trichloro-1-nitrobutane[g]	3″	cl	01	6.26	7.47	..	..	..	...	...	...	...
$C_4H_5N_3O_4$	3-Nitro-4-ethylfuroxane[g]	BF	l	03	6.65	7.36	..	..	..	...	...	...	6.12, 6.36[h]
$C_4H_7NO_2$	1-Nitro-1-butene (*trans*)	0 II	l	01	6.55	7.37	..	..	..	...	...	...	6.05, 10.41[d]
$C_4H_7NO_2$	1-Nitro-2-butene (*trans*)[g]	1 II	l	03	6.43	7.27	6.99	..	..	...	...	...	5.96, 10.39[d]
$C_4H_7NO_2$	1-Nitro-2-methyl-1-propene	0 IV	cl	01	6.58	7.38	..	..	..	...	...	...	6.06, 12.16[d]
$C_4H_7NO_2$	1-Nitro-2-methyl-2-propene	1 III	l	03	6.41	7.26	6.99	..	..	...	...	...	6.02, 10.85[d]
$C_4H_7NO_2$	1-Nitro-1-methylcyclopropane[g]	3	l	03	6.50	7.37	..	..	..	...	...	...	7.17[p]
$C_4H_8N_2O_3$	1-Nitro-2-butanone oxime[g]	1′ II	l	03	6.40	7.28	7.06	..	..	...	...	...	6.04,[i] 10.73[j]
$(C_4H_8N_2O_3)_2$	Bis-(1-nitro-2-nitrosobutane)	1 D	s	03	6.38	7.25	7.06	..	..	...	...	...	7.18, 8.29[k]
$C_4H_8N_2O_3$	1-Nitro-2-nitroso-2-methylpropane	1	te	05	6.38	7.26	7.04	..	..	...	...	...	...
$(C_4H_8N_2O_3)_2$	Bis-(1-nitro-2-nitroso-2-methylpropane)	1 D	s	03	6.43	7.24	7.02	..	..	...	...	...	7.87[k]
$C_4H_8N_2O_4$	1,2-Dinitrobutane	1,2	l	03	6.38	7.23	7.07	..	..	...	...	...	...
$C_4H_8N_2O_4$	1,2-Dinitro-2-methylpropane	1,3	l	03	6.45	7.43	7.06	..	..	...	...	...	7.18[l,n]
$C_4H_8N_2O_5$	1,1-Dinitro-3-butanol[g]	2′	l	03	6.35	7.51	..	..	..	...	...	...	7.24[l]
$C_4H_8N_2O_5$	1-Nitro-2-butyl nitrate[g]	1 N	l	03	6.41	7.24	7.05	6.09	7.84	11.78	13.29	14.41	...
$C_4H_8N_2O_5$	1-Nitro-3-butyl nitrate[g]	1 N	l	03	6.42	7.24	7.00	6.09	7.84	11.62	13.25	14.33	...
$C_4H_8N_2O_5$	2-Nitrobutyl nitrate[g]	2 N	l	03	6.43	7.32	..	6.06	7.83	11.85	13.30	14.50	...
$C_4H_8N_2O_5$	1-Nitro-2-methyl-2-propyl nitrate	1 N	l	03	6.43	7.25	6.98	6.09	7.70	11.7	13.29	14.11	...
$C_4H_9NO_2$	2-Nitro-2-methylpropane	3	l	03	6.48	7.43	..	..	..	...	...	...	[n]
$C_4H_9NO_3$	1-Nitro-2-butanol	1	l	03	6.43	7.23	7.02	..	..	...	...	...	...
$C_4H_9NO_3$	2-Nitrobutanol	2	l	03	6.45	7.33	..	..	..	...	...	...	...

TABLE I (*Continued*)

Empirical formula	Name	Type[a]	State[b]	Accuracy[c]	Bands of group								Miscellaneous
					NO_2	NO_2	CH_2	ONO_2	ONO_2	ONO_2	ONO_2	ONO_2	
$C_4H_9NO_3$	1-Nitro-2-methyl-2-propanol	1	l	03	6.41	7.23	6.99	..	..	...	...	...	...
$C_4H_9NO_4$	2-Hydroxy-2-methylpropyl nitrate[g] (?)	N	l	03	..	..	..	6.10	7.79	11.47	13.22	14.40	...
$C_4H_{10}N_2O_3$	N-(1-Nitro-2-methyl-2-propyl)-hydroxylamine[g]	1 H	l	03	6.43	7.28	7.02	..	..	...	...	...	11.55[j]
$C_5H_8N_2O_2$	4-Propylfuroxane[g] (?)	F	l	03	..	..	..	..	..	...	...	...	6.19, 6.35 ?[f,h]
$C_5H_7N_3O_4$	3-Nitro-4-propylfurazoxane	BF	l	03	6.64	7.36	..	..	..	...	...	...	6.12,[f,h]
$(C_5H_9NO)x$	Poly-(3-nitroso-2-methyl-2-butene)	H	l	03	..	..	..	..	..	...	...	...	6.10,[i] 10.6[j]
$C_5H_9NO_2$	2-(Nitromethyl)-1-butene[g]	1 IV	l	03	6.41	7.24	6.16	..	..	...	...	...	..,[f] 10.83[d]
$C_5H_9NO_2$	1-Nitro-2-methyl-2-butene	1 IV	l	03	6.43	7.27	6.99	..	..	...	...	...	5.95, 12.50[d]
$C_5H_9NO_2$	1-Nitro-2-methyl-1-butene[g]	0 IV	l	03	6.58	7.43	..	..	..	...	...	...	6.07, 12.00[d]
$C_5H_9NO_2$	3-Nitro-2-methyl-1-butene[g]	2 III	l	03	6.46	7.36	..	..	..	...	...	...	6.05, 10.92[d]
$C_5H_9NO_2$	3-Nitro-2-methyl-2-butene	0 V	l	03	6.60	7.46	..	..	..	...	...	...	6.01[d]
$C_5H_9NO_2$	1-Nitro-1-pentene (*trans*)	0 II	cl	01	6.55	7.41	..	..	..	...	...	...	6.01, 10.43[d]
$C_5H_9NO_2$	1-Nitro-2-pentene (*trans*)[g]	1 II	l	05	6.48	7.29	7.02	..	..	...	...	...	6.01, 10.36[d]
$C_5H_{10}N_2O_3$	3-Nitro-2-nitroso-2-methylbutane	2	cl	03	6.44	7.36	..	..	..	...	...	...	...
$(C_5H_{10}N_2O_3)_2$	Bis-(3-nitro-2-nitroso-2-methylbutane)	2 D	s	03	6.44	7.34	..	..	..	...	...	...	7.82[k]
$(C_5H_{10}N_2O_3)_2$	Bis-(1-nitro-2-nitrosopentane)[g]	1 D	l	03	6.42	7.28	6.98	..	..	...	...	...	7.18, 8.33[k]
$C_5H_{10}N_2O_3$	1-Nitro-2-pentanone oxime[g]	1′ H	l	05	6.44	7.28	7.07	..	..	...	...	...	6.16 ?,[i] 10.63[j]
$C_5H_{10}N_2O_4$	1,3-Dinitro-2,2-dimethylpropane	1	l	03	6.44	7.27	7.01	..	..	...	...	...	...
$C_5H_{10}N_2O_4$	2,3-Dinitro-2-methylbutane	2, 3	l	03	6.45	7.44	..	..	..	...	...	...	7.28[l,n]
$C_5H_{10}N_2O_5$	3-Nitro-2-methyl-2-butyl nitrate	2 N	l	03	6.43	7.32	..	6.11	7.72	11.73	13.24	14.09	...
$C_5H_{11}NO_2$	2-Nitro-2-methylbutane	3	cl	01	6.50	7.39	..	..	..	...	...	...	[n]
$C_5H_{11}NO_2$	1-Nitropentane[o]	1	cl	01	6.44	7.23	6.96	..	..	...	...	...	...
$C_5H_{11}NO_2$	2-Nitropentane	2	l	03	6.44	7.33	..	..	..	...	...	...	7.18[p]
$C_5H_{11}NO_3$	*t*-Amyl nitrate	N	l	03	..	..	..	6.12	7.82	11.65	13.20	14.35	...
$C_5H_{11}NO_3$	1-Nitro-2-methoxybutane[g]	1	l	03	6.45	7.25	7.00	..	..	...	...	...	...
$C_5H_{11}NO_3$	1-Nitro-2-methoxy-2-methylpropane[g]	1	l	03	6.43	7.27	7.01	..	..	...	...	...	...
$C_5H_{11}NO_3$	1-Nitro-2-methyl-2-butanol	1	l	03	6.42	7.24	7.00	..	..	...	...	...	...
$C_5H_{11}NO_3$	2-Nitro-2-methyl-3-butanol	3	l	03	6.48	7.39	..	..	..	...	...	...	[n]
$C_5H_{11}NO_3$	3-Nitro-2-methyl-2-butanol	2	l	03	6.45	7.35	..	..	..	...	...	...	...
$C_5H_{11}NO_3$	1-Nitro-2-pentanol	1	l	05	6.47	7.25	7.08	..	..	...	...	...	...
$C_5H_{11}NO_3$	2-Pentyl nitrate[g]	N	l	05	..	..	..	6.13	7.82	11.53	13.19	14.35	...
$C_6ClH_4NO_2$	*p*-Chloronitrobenzene	B	cl	01	6,55	7.41	..	..	..	...	...	...	[q]
$C_6ClH_{10}NO_3$	2-Chlorocyclohexyl nitrate (*trans*)[g]	N	l	03	..	..	..	6.10	7.83	11.67	13.43	14.41	...
$C_6Cl_2H_{11}NO_3$	1,1-Dichloro-2-ethoxy-1-nitrobutane[g]	3″	l	03	6.33	7.51	..	..	..	...	...	...	...
$C_6H_4N_2O_4$	*m*-Dinitrobenzene	B	cl	01	6.46	7.39	..	..	..	...	...	...	[q]
$C_6H_5NO_2$	Nitrobenzene	B	cl	01	6.54	7.39	..	..	..	...	...	...	[q]
$C_6H_5NO_3$	*p*-Nitrophenol	B	cl	01	6.56	7.43	..	..	..	...	...	...	[q]
$C_6H_6N_2O_2$	*m*-Nitroaniline	B	cl	01	6.55	7.37	..	..	..	...	...	...	[q]
$C_6H_6N_2O_2$	*p*-Nitroaniline	B	cl	01	6.63	7.46	..	..	..	...	...	...	[q]
$(C_6H_7N_3O_{11})_x$	Cellulose nitrate	N	cl	03	..	..	..	5.99	7.81	11.89	[f]	14.38	...
$(C_6H_8N_2O_3)_2$	Bis-(2-nitro-2-nitrosobicyclo[3.1.0]hexane[g]	3′D	s	03	6.38	7.31 or 7.61		..	..	...	...	...	7.85[k]
$C_6H_9NO_2$	2-Nitrobicyclo[3.1.0]hexane[g]	2	l	03	6.46	7.27	..	..	..	...	...	...	...
$C_6H_9NO_2$	1-Nitrocyclohexene	0 IV	l	03	6.61	7.48	..	..	..	...	...	...	5.98, 12.15 ?[d]

TABLE I (*Continued*)

Empirical formula	Name	Type[a]	State[b]	Accuracy[c]	Bands of group								Miscellaneous
					NO_2	NO_2	CH_2	ONO_2	ONO_2	ONO_2	ONO_2	ONO_2	
$C_6H_9NO_2$	3-Nitrocyclohexene	2 II	l	03	6.45	7.32	..	..	..	...	...	...	6.02, >15[d,m]
$C_6H_9NO_2$	4-Nitrocyclohexene[g]	2 II	l	03	6.46	7.27	..	..	..	...	...	...	6.02, ~15[d]
$C_6H_9NO_2$	1-(Nitromethyl)-cyclopentene	1 IV	l	03	6.43	7.27	7.01	..	..	...	...	...	6.03, 12.05[d]
$C_6H_9NO_3$	2-Nitrocyclohexanone[g] (?)	2′	l	03	6.34	7.26 or 7.61		..	..	...	...	...	5.75[l]
$(C_6H_{10}N_2O_3)_2$	Bis-(1-nitro-2-nitrosocyclohexane) (*cis*)	2 D	s	03	6.42	7.25	..	..	..	...	...	...	7.15, 8.31[k]
$(C_6H_{10}N_2O_3)_2$	Bis-(1-nitro-2-nitrosocyclohexane) (*trans*)	2 D	s	03	6.43	7.25	..	..	..	...	...	...	7.16, 8.24[k]
$C_6H_{10}N_2O_4$	1,1-Dinitrocyclohexane	3′	cl	01	6.36	7.56	..	..	..	...	...	...	7.26[l]
$C_6H_{10}N_2O_4$	3,4-Dinitro-3-hexene (*trans*)[r]	0′ V	s	03	6.47	7.4	..	..	..	...	...	...	No C=C band
$(C_6H_{10}N_2O_4)_2$	Bis-(2-nitrosocyclohexyl nitrate) (*trans*)	D N	s	03	..	..	..	6.12	7.87	11.47	13.28	14.54	7.18, 8.33[k]
$C_6H_{10}N_2O_5$	2-Nitrocyclohexyl nitrate (*cis*)[g]	2 N	l	03	6.46	7.28	..	6.10	7.86	11.56	13.33	14.52	...
$C_6H_{10}N_2O_5$	2-Nitrocyclohexyl nitrate (*trans*)	2 N	l	03	6.43	7.26	..	6.08	7.84	11.50	13.35	14.50	...
$C_6H_{10}N_2O_5$	3-Nitrocyclohexyl nitrate (*trans*)[g]	2 N	l	03	6.44	7.25	..	6.12	7.83	11.50	13.25	14.43	...
$C_6H_{10}N_2O_5$	4-Nitrocyclohexyl nitrate (*cis*)[g]	2 N	l	03	6.46	7.24	..	6.13	7.83	11.55	13.23	14.41	...
$C_6H_{10}N_2O_5$	4-Nitrocyclohexyl nitrate (*trans*)[g]	2 N	s	03	6.50	7.26	..	6.12	7.83	11.45	13.22	14.28	...
$C_6H_{10}N_2O_5$	1-(Nitromethyl)-cyclopentyl nitrate[g]	1 N	l	03	6.43	7.28	7.02	6.12	7.78	11.70	13.31	14.23	...
$C_6H_{11}NO$	Cyclohexanone oxime	H	ct	05	..	..	..	..	..	...	...	...	6.00,[i] 10.58 (?)[i]
$C_6H_{11}NO_2$	Nitrocyclohexane	2	l	03	6.46	7.26	..	..	..	...	...	...	...
$C_6H_{11}NO_2$	1-Nitro-2,3-dimethyl-1-butene[g]	0 IV	l	05	6.62	7.43	..	..	..	...	...	...	6.11, 12.07[d]
$C_6H_{11}NO_2$	1-Nitro-2,3-dimethyl-2-butene[g]	1 V	l	03	6.45	7.31	6.98	..	..	...	...	...	5.98[d]
$C_6H_{11}NO_2$	3-Nitro-2,3-dimethyl-1-butene[g]	3 III	l	03	6.49	7.43	..	..	..	...	...	...	6.06, 10.99[d]
$C_6H_{11}NO_2$	2-(Nitromethyl)-3-methyl-1-butene[g]	1 III	l	05	6.46	7.32	7.01	..	..	...	...	...	6.05, 10.84[d]
$C_6H_{11}NO_3$	Cyclohexyl nitrate	N	l	03	..	..	..	6.15	7.83	11.50	13.19	14.40	...
$C_6H_{11}NO_3$	2-Nitrocyclohexanol (*cis*)[g]	2	l	03	6.45	7.25	..	..	..	...	...	...	...
$C_6H_{11}NO_3$	2-Nitrocyclohexanol (*trans*)	2	l	03	6.45	7.27	..	..	..	...	...	...	...
$C_6H_{11}NO_3$	1-(Nitromethyl)-cyclopentanol[g]	1	l	03	6.45	7.23	7.03	..	..	...	...	...	...
$C_6H_{11}NO_4$	1,2-Cyclohexanediol mononitrate (*trans*)[g]	N	l	03	..	..	..	6.14	7.86	11.55	13.22	14.30	...
$C_6H_{11}NO_4$	1-Nitro-2-butyl acetate	1	l	03	6.40	7.27	7.01	..	..	...	...	...	...
$C_6H_{12}N_2O_4$	2,3-Dinitro-2,3-dimethylbutane	3	cl	03	6.47	7.44	..	..	..	...	...	...	[n]
$C_6H_{12}N_2O_4$	2,2-Bis-(nitromethyl)-butane	1	l	03	6.44	7.27	7.01	..	..	...	...	...	...
$C_6H_{13}NO_2$	2-Methoxy-2-methyl-3-butanone oxime	H	s	03	..	..	..	..	..	...	...	...	6.06,[i] 10.70[i]
$C_7ClH_4NO_3$	*p*-Nitrobenzoyl chloride	B	cl	01	6.51	7.40	..	..	..	...	...	...	[q]
$C_7H_5NO_3$	*m*-Nitrobenzaldehyde	B	cl	01	6.49	7.37	..	..	..	...	...	...	[q]
$C_7H_7NO_2$	*m*-Nitrotoluene	B	cl	01	6.53	7.38	..	..	..	...	...	...	[q]
$C_7H_7NO_2$	*p*-Nitrotoluene	B	cl	01	6.56	7.40	..	..	..	...	...	...	[q]
$C_7H_7NO_2$	Phenylnitromethane	1	l	03	6.42	7.28	6.97	..	..	...	...	...	13.97[s]
$C_7H_7NO_3$	Benzyl nitrate	N	l	03	..	..	..	6.10	7.79	11.62	13.19	14.34	...
$C_7H_7NO_3$	*p*-Nitroanisole	B	cl	01	6.60	7.43	..	..	..	...	...	...	[q]
$C_7H_{13}NO_3$	4-Nitro-3-hepten-5-ol	0 IV	l	03	6.58	7.45	..	..	..	...	...	...	6.02, 12.73 ?[d]
$C_7H_{13}NO_4$	3-Nitro-2-methyl-2-butyl acetate[g]	2	l	03	6.43	7.31	..	..	..	...	...	...	...
$C_7H_{14}N_2O_3$	*O*-(1-Nitro-2-methyl-2-propyl) acetoxime[g]	1 H	l	03	6.45	7.29	7.03	..	..	...	...	...	6.05,[i] 10.57[i]
$C_8Cl_2H_7NO_2$	1,2-Dichloro-1-nitro-2-phenylethane	2′	l	03	6.36	7.45	..	..	..	...	...	...	...
$C_8H_7NO_2$	1-Nitro-2-phenylethylene (*trans*)	0 II	l	03	6.59	7.46	..	..	..	...	...	...	6.11, 10.30[d]
$C_8H_9NO_2$	1-Nitro-1-phenylethane	2	l	03	6.46	7.35	..	..	..	...	...	...	13.94[s]

TABLE I (*Continued*)

Empirical formula	Name	Type[a]	State[b]	Accuracy[c]	Bands of group								Miscellaneous
					NO_2	NO_2	CH_2	ONO_2	ONO_2	ONO_2	ONO_2	ONO_2	
$(C_8H_{12}N_2O_3)_2$	Bis-(1-nitro-2-nitroso-2(cyclohexen-4-yl)-ethane)[g]	1 D	s	03	6.39	7.29	7.09	..	..	...	...	...	7.14, 8.34[k]
$C_8H_{15}NO_2$	1-Nitro-1-octene (*trans*)	0 II	l	03	6.54	7.39	..	..	..	...	...	...	6.04, 10.44[d]
$C_8H_{15}NO_2$	1-Nitro-2-octene (*trans*)[g]	1 II	l	03	6.42	7.27	6.98	..	..	...	...	...	5.97, 10.31[d]
$(C_8H_{16}N_2O_3)_2$	Bis-(1-nitro-2-nitrosoöctane)[g]	1 D	s	03	6.39	7.25	7.05	..	..	...	...	...	7.17, 8.32[k]
$(C_8H_{16}N_2O_3Si)_2$	Bis-(1-nitro-2-nitroso-3-propyldimethylallyl silane)[g]	1 D	cl	03	6.40	7.28	..	..	..	...	...	...	7.21 (?)[f,k]
$C_8H_{16}N_2O_5$	Di-(1-nitro-2-methyl-2-propyl) ether (?)[g]	1	s	03	6.46	7.28	6.96	..	..	...	...	...	...
$C_8H_{16}N_2O_5$	1,1-Dinitro-3-octanol[g]	2′	l	03	6.32	7.50	..	..	..	...	...	...	7.24[l]
$C_8H_{16}N_2O_5$	1-Nitro-3-octyl nitrate[g]	1 N	l	03	6.42	7.25	6.96	6.10	7.84	11.59	13.25	14.42	...
$C_8H_{17}NO_3$	1-Nitro-2-octanol[g]	1	l	03	6.42	7.25	7.04	..	..	...	...	...	...
$C_8H_{17}NO_3$	2-Octyl nitrate	N	l	03	..	..	..	6.12	7.83	11.8	13.20	14.30	...
$C_8H_{17}N_3O_5$	*O,N*-Bis-(1-nitro-2-methyl-2-propyl)-hydroxylamine[g]	1 H	l	03	6.42	7.25	6.98	..	..	...	...	...	11.55[j]
$(C_8H_{20}N_2O_4Si)_2$	Bis-(1-nitro-2-nitroso-3-propylpentamethyldisiloxane)[g]	1 D	cl	03	6.41	7.29	..	..	..	...	...	...	7.21 (?)[f,n]
$C_9H_9NO_2$	1-(Nitromethyl)-1-phenylethylene[g]	1 IV	l	03	6.43	7.28	6.97	..	..	...	...	...	[f], 10.87[d]
$C_9H_9NO_2$	1-Nitro-2-phenyl-1-propene[g]	0 IV	l	03	6.61	7.46	..	..	..	...	...	...	6.13 (?), 11.96[d]
$C_9H_{11}NO_2$	2-Nitro-2-phenylpropane	3	l	03	6.47	7.40	..	..	..	...	...	...	13.94[s,n]
$C_{10}H_{13}NO_2$	1-Nitro-2,2-dimethyl-2-phenylethane	1	l	03	6.42	7.28	6.98	..	..	...	...	...	...
$C_{10}H_{13}NO_2$	2-Nitro-2,2-dimethyl-1-phenylethane (?)[g]	3	l	03	6.51	7.40	..	..	..	...	...	...	[n]
$C_{10}H_{16}N_2O_3$	1-Nitrocarvenone oxime	3′ H VI	s	03	6.43	7.48	..	..	..	...	...	...	6.07,[i] 6.13,[d] 10.43,[j] 12.36[d]
			ac	03	6.46	[f]	..	..	..	...	...	...	6.09,[d,i] 10.34,[j] 12.36[d]
$C_{12}H_{3}N_5O_7$	4-Ketocyclohexyl nitrate 2,4-dinitrophenylhydrazone[g]	BN	cl	03	6.63	7.48	..	6.15	7.83	11.66	[f]	[f]	...

[a] Key: 1, 2, 3 are, respectively, primary, secondary and tertiary nitro compounds; "′" indicates that there is present on the carbon holding the nitro group a negative, or electron-withdrawing, substituent, such as Cl, Br, NO, NO_2 or $-C(=O)R$; O, conjugated nitroalkenes; B, aromatic or heterocyclic nitro compounds; H, hydroxylamine or oxime; D, nitroso dimer compound; N, nitrate ester; F, furoxane. Olefin type, where X represents all groups other than hydrogen; I, $XCH=CH_2$; II, $XCH=CHX$; III, $X_2C=CH_2$; IV, $X_2C=CHX$; V, $X_2C=CS_2$. [b] Key: l, liquid; s, solid; cl, chloroform solution; te, tetrachloroethylene solution; ct, carbon tetrachloride solution; ac, acetone solution. [c] Maximum error × $10^2\mu$. [d] Olefin C=C stretching and C=CH wagging bands. [e] Data furnished by Prof. L. B. Clapp. [f] Band position obscured by impurities, solvent or stronger bands of compounds. [g] New compound; preparation and proof of structure to be published. [h] Furoxane bands. [i] C=N stretching band. [j] N–O stretching band. [k] Bisnitroso group bands. [l] Second NO_2 symmetrical stretching band. [m] Additional bands, see Table IV. [n] Additional bands, see Table III. [o] Sample furnished by Prof. G. B. Bachman. [p] Methyl band in CH_3-C-NO_2. [q] Additional bands, see Fig. 2. [r] Sample furnished by Prof. L. B. Clapp. [s] Bands of $C_6H_5-C-NO_2$ structure. [t] Carbonyl stretching band.

TABLE II

INFRARED BANDS IN COMPOUNDS CONTAINING THE $-NO_2$ GROUP[a]

No.	Compound type[b]	No. cpds. examined	NO_2 asym. str., μ	NO_2 sym. str., μ
1	$RONO_2$	21	6.10 ± 0.05	7.82 ± 0.04
2	Cl_3CNO_2	1	6.21	7.62
3	RCl_2CNO_2	3	6.30 ± .04	7.51 ± .04
4	$RCH(NO_2)_2$	4	6.32 ± .03	7.50 ± .02
5	$RXCHNO_2$ (X = Cl, Br)	4	6.35 ± .02	7.42 ± .03
6	$R_2C(NO_2)_2$	2	6.36	7.54 ± .02
7	CH_3NO_2	1	6.38	7.26
8	R_2CClNO_2	1	6.39	7.45
9	RCH_2NO_2	38	6.42 ± .03	7.27 ± .04
10	R_2CHNO_2	20	6.45 ± .02	7.30 ± .06
11	R_3CNO_2	10	6.49 ± .02	7.41 ± .04
12	$RC(NO_2){=}C(NO_2)R$	1	6.47	7.4
13	$RHC{=}CClNO_2$	1	6.47	7.51
14	$ArNO_2$	12	6.55 ± .08	7.42 ± .06
15	$C{=}CNO_2$[c]	5	6.56 ± .02	7.39 ± .03
16	$C{=}CNO_2$[d]	7	6.60 ± .02	7.43 ± .05
17	$RC(NO_2)_2K$	1	8.05	8.69

[a] Ranges of observed band positions in the liquid phase, based on individual measurements which were accurate to ±0.03 μ or better. [b] R is alkyl, alkenyl or aromatic. [c] Nitro derivatives of ethylene and monoalkyl ethylenes. [d] Nitro derivatives of di- and trialkyl ethylenes.

TABLE III

INFRARED BANDS IN $XC(CH_3)_2NO_2$ COMPOUNDS

X	Observed infrared bands			
H	7.14	7.28	7.35	11.76
CH_3	7.12	7.29	7.43	11.66
C_2H_5	7.16	7.29	7.39	11.68
$CH(OH)CH_3$	7.14	7.27	7.39	11.67
CH_2NO_2	7.15	7.28	7.43	11.61
$C(CH_3)HNO_2$	7.13	7.28	7.44	11.74
$C(CH_3)_2NO_2$	7.17	7.26	7.45	11.75
C_6H_5	7.15	7.27	7.40	11.75
C_3H_5	7.20	7.26	7.43	11.79
Cl	7.16	7.26	7.45	11.78
NO_2	7.11	7.26	7.37, 7.52	11.69, 11.83

has been observed in tetranitromethane.[3] In the *gem*-dinitro compounds which we studied, there was no splitting of the NO_2 asymmetrical stretching band (single band of normal half-intensity band width) but splitting of the NO_2 symmetrical stretching band appeared to occur. 1,1-Dinitrocyclohexane, for example, showed bands at 7.26 and 7.56 μ. In such cases, the stronger of the two bands has arbitrarily been listed as the NO_2 symmetrical stretching band in Table II.

Vibrational interaction also occurs with methyl groups. Normally, the symmetrical C–H bending vibration of C-methyl groups and the symmetrical NO_2 stretching vibrations of the simple nitroalkanes both give bands near 7.25 μ. When methyl and nitro groups are attached to the same carbon, however, splitting rather than coincidence of the bands is observed. In compounds containing the CH_3–C–NO_2 structure, the observed bands lie near 7.17 and 7.3 μ. Compounds containing the $(CH_3)_2$–C–NO_2 structure show bands at 7.16 ± 0.04, 7.28 ± 0.02, 7.40 ± 0.05 and 11.72 ± 0.11 μ.

This pattern of strong bands is highly characteristic of the $(CH_3)_2$–C–NO_2 structure, and appears to be little affected by the mass or electrical character of the other group attached to the structure, as may be seen from Table III.

Nitro groups may also produce shifts in the characteristic infrared bands of the groups to which they are attached. In the α-nitro ketones, both the carbonyl stretching and the NO_2 asymmetrical stretching bands are shifted to shorter wave lengths. The primary nitro compounds, like the α-methylene ketones and esters, show an "active methylene" band at 7.00 ± 0.05 μ. This band is a valuable adjunct to the 6.42 ± 0.03 μ band in the identification of primary nitro compounds. Lastly, the three compounds we examined which had the C_6H_5–C–NO_2 grouping all showed a prominent band near 13.95 μ, which may be characteristic for that structure.

Nitroalkenes.—The conjugated nitroalkenes show NO_2 asymmetrical stretching bands at 6.45–6.65 μ (*E ca.* 400) and NO_2 symmetrical stretching bands at 7.35–7.5 μ (*E ca.* 300). The exact positions of these bands are determined by the nature of the substituents present on the olefinic carbons, as shown in Table II. It is noteworthy that the symmetrical stretching band is nearly as strong as the asymmetrical, although in the nitroalkanes it is only about a quarter as strong. As with the nitroalkanes, no consistent behavior in the 10–12 μ region which might be attributed to C–N stretching bands could be observed. Even in the case of nitroethylene, where all but two or three of the observed infrared bands could be accounted for as known vibrations of the nitro and vinyl groups, an empirical assignment of the C–N stretching mode did not seem justifiable.

It is well known that the various types of substituted ethylenes may be distinguished from one another by the characteristic patterns of their C=C stretching, C–H stretching and C–H wagging bands.[4,5] It is also known, however, that these patterns may be altered somewhat if non-hydrocarbon substituents are present either on the double bond, or on the carbon adjacent to it.[6] The behavior of the nitro group in this regard is shown in Table IV.

Table IV indicates that on the whole the nitro group has surprisingly little effect upon the positions of the characteristic olefinic C–H and C=C bands. The C=C stretching band is intensified, however, in both the α- and the β-nitro olefins; and the olefinic C–H stretching and wagging bands are intensified when the nitro group is on the same carbon as the olefinic hydrogen.

Aromatic Nitro Compounds.—It has been previously reported that aromatic nitro compounds show bands at 6.59 ± 0.05 and 7.41 ± 0.05 μ due to NO_2 stretching, and at 11.78 ± 0.12 μ due to C–N

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(3) P. H. Lindenmeyer and P. M. Harris, *J. Chem. Phys.*, **21**, 408 (1953).

(4) H. L. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

(5) N. Sheppard and D. M. Simpson, *Quart. Revs.*, **6**, 1 (1952).

(6) R. S. Rasmussen in "Progress in the Chemistry of Natural Products," Springer Verlag, Vienna, 1948, p. 353.

TABLE IV

SOME INFRARED BANDS OF MONONITRO OLEFINS

Olefin type[a]	Substituents X[b]	No. cpds. examined	H—C str.	C=C str.	H—C wag.
$XCH{=}CH_2$	R[b]	7[c]	3.24, 3.32, 3.36	6.07–6.09	10.00–10.08, 10.88–11.02
	CNO_2[b]	1	3.22, 3.29	6.07	10.09, 10.57
	NO_2	1	3.21, 3.29, 3.35	6.09	10.36, 10.64
$XCH{=}CHX$ (*trans*)	R	9[c]	3.30–3.32	(5.97–6.00)[d]	10.22–10.38
	R, CNO_2[b]	3	3.28–3.32	5.96–6.01	10.31–10.39
	R, NO_2	5	3.22–3.28	6.04–6.07[e]	10.40–10.44[e]
$XCH{=}CHX$ (cyclohexene)	R	..[f]		6.06–6.07	*ca.* 15
	R, CNO_2[b]	1	3.30	6.02	15
$X_2C{=}CH_2$	R	7[c]	3.23–3.25	6.02–6.10	11.21–11.26
	R, CNO_2[b]	5	3.24–3.28	6.02–6.06	10.83–10.99
	R, NO_2	3[g]	3.14–3.19	5.97–6.00	10.61–10.67
$X_2C{=}CHX$	R	6[c]	3.29–3.31	5.95–6.01	12.0–12.5
	R, CNO_2[b]	2	3.28	5.95–6.03	12.05–12.50
	R, NO_2[h]	5	3.26–3.28	6.06–6.11	11.96–12.16
	R, NO_2[i]	2	3.26	5.97–6.02	?
$X_2C{=}CX_2$	R	2[c]	..	(5.98–6.00)[d]	....
	R, CNO_2[b]	1	..	5.98	....
	R, NO_2	1	..	6.01	....

[a] X represents all substituents other than hydrogen. [b] R represents an alkyl radical; CNO_2 represents an α-nitroalkyl radical. [c] Data taken from reference 5. [d] From Raman data; band is infrared inactive. [e] Further conjugation produces further band shifts to 6.11 and 10.30 μ in ω-nitrostyrene. [f] Data taken from reference 6, p. 351. [g] Data supplied by Dr. K. S. McCallam. [h] Compounds of type $R_2C{=}CHNO_2$. [i] Compounds of type $RHC{=}CRNO_2$.

stretching.[7] Our infrared spectra of nitrobenzenes in chloroform solution all showed strong NO stretching bands of variable intensity at 6.46–6.63 and 7.37–7.46 μ.

In hopes of recognizing further correlations among the nitrobenzene spectra, all of the observed bands in the 2–12.5 μ regions of the spectra were plotted against the Hammett σ-values of the substituents. The plot showed that the bands near 6.2 and 6.3 μ arising from benzene ring vibrations varied independently of either the orientation or the σ-value, while the positions of the bands near 6.7 μ were at least roughly related to σ, as shown in Fig. 2. These bands were stronger in the *p* than in the *m* derivatives, and became stronger at the more negative values of σ. The NO_2 asymmetrical stretching bands showed a good linear correlation with σ, also shown in Fig. 2, the wave lengths being lengthened by substituents having more negative sigmas. The wave lengths of the NO_2 symmetrical stretching bands, however, were lengthened by either negative or positive substituents. Over most of the observed range, the intensities[8] of the NO_2 stretching bands fluctuated independently of σ; however, at the more negative σ-values, the asymmetrical stretching bands did tend to become weaker and the symmetrical stretching bands stronger. The bands in the 7.5–12.5 μ region were dependent largely upon the orientation of the substituent; the *m* compounds gave one pattern of bands, while the *p* compounds gave another.

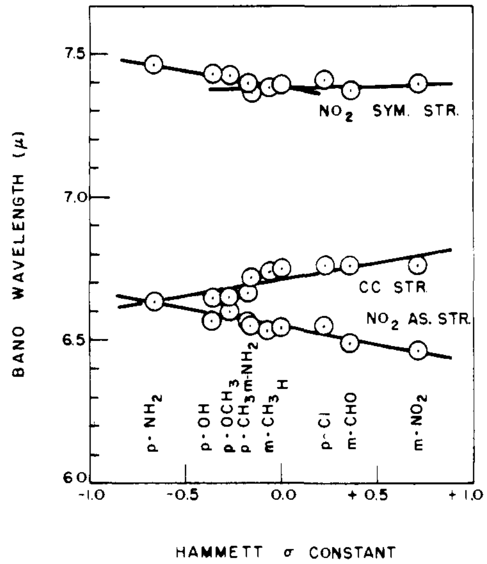

Fig. 2.—Correlation between σ-constant and band positions in *m*- and *p*-substituted nitrobenzenes.

In hopes of verifying the previous assignments for the C–N stretching mode,[7] particular attention was given to the 11.8 μ region. The *p*-substituted derivatives all showed a pair of prominent, σ-independent bands at 11.55–11.70 and 11.75–11.95 μ, and it is to one or the other of these bands that most of the previous assignments for the C–N stretching mode refer. However, since the bond orders of the C–N bonds in substituted nitrobenzenes are certainly strongly σ dependent, such assignments must be incorrect. *m*-Nitrobenzaldehyde showed no bands at all in the 11.1–12.2 μ region, and the other *m* substituted nitrobenzenes showed only scattered weak bands in this range.

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(7) R. R. Randle and D. H. Whiffen, *J. Chem. Soc.*, 4153 (1952).

(8) Both the apparent molecular extinction coefficients and the apparent integrated absorption intensities were considered. The latter were roughly estimated as the products of the former and the apparent half-intensity bands widths. Exact determinations of the integrated absorption intensities were hindered by the proximity of other spectral bands, and by the fact that both the NO_2 stretching bands are too narrow to permit the use of the tables given by D. A. Ramsay, THIS JOURNAL, **74**, 72 (1952).

It is concluded, therefore, that the location of the C–N stretching band in aromatic nitro compounds is still unknown.

Nitrate Esters.—Nitrate esters showed very strong (*E ca.* 600–650) infrared bands at 6.1 and 7.8 μ, a broader and weaker (*E ca.* 300) band near 11.7 μ, and bands of medium intensity near 13.3 and 14.3 μ. These bands are quite similar to those found in nitric acid, and it seems likely that similar vibrational assignments can be made, as shown in Table V.

TABLE V

INFRARED BANDS IN NITRATE ESTERS

$RONO_2$ bands (μ)[a] (liquid phase)	$HONO_2$ bands (μ)[b] (liquid; vapor)	Assignment[b]
6.10 ± 0.05vs	6.00; 5.85	NO_2 asym. str.
7.82 ± .04vs	7.70; 7.58	NO_2 sym. str.
11.68 ± .21s	10.87; 11.29	O'N str.
13.29 ± .14m	13.03; 13.08	Out of plane
14.30 ± .22m[c]	14.77; 14.77	NO_2 bending
............[d]	16.40; 17.16	O'NO bending

[a] Normal ranges of band positions for liquid mononitrates. [b] C. Fréjacques, *Compt. rend.*, **234**, 1769 (1952); H. Cohn, C. K. Ingold and H. G. Poole, *J. Chem. Soc.*, 4272 (1952). [c] J. C. D. Brand and T. Cawthon (private communication) suggest that the band near 14.3 μ is actually an overtone of the 351 cm.$^{-1}$ C–O–N bending band, while the true NO_2 bending band comes near 17 μ. The 14.3 μ band is not shown by methyl nitrate. [d] The instrument used in this work permitted measurements only up to 15 μ.

Because of the strength and consistency of the spectra, nitrate esters are easily and unambiguously identified, even in mixtures with large amounts of other polar compounds. We were unable, however, to find any way of distinguishing between primary, secondary and tertiary nitrates from the infrared spectra. In a few types of nitrates, small extensions of the ranges of band positions given in Table V are needed. Thus, the spectra of cellulose nitrate and of some other polyol nitrates[9] indicate that in polynitrates the asymmetrical stretching band may appear as low as 6.0 μ, and the O'N stretching band as high as 12.0 μ. In 1-nitro-2-methyl-2-propyl nitrate and one or two similar substances, the 7.82 μ band appears to have been shifted to shorter wave lengths; this shift may actually be a band splitting, however, since the 7.70 μ band is accompanied by another fairly strong one at 7.91 μ.

Bisnitroso Compounds.—No theoretical vibrational analyses for bisnitroso compounds (nitroso dimers) have been reported. Ourisson[10] noted that the secondary bisnitroso compound, bis-(methyl 10-nitroso-11-nitroundecoate), had bands at 8.38 and 9.10 μ which were absent from the spectrum of the corresponding oxime. The Raman spectrum of a solution which probably contained both monomeric and dimeric 2-nitroso-2-methyl-3-butanone indicated that the tertiary bisnitroso compound may have given shifts corresponding to infrared wave lengths of 6.20, 6.44, 7.76 or 8.72 μ.[11]

Our examination of the infrared spectra of seven secondary bisnitroso compounds in the solid phase showed that all had a band of generally medium intensity at 7.16 ± 0.02 μ, and a strong band at 8.29 ± 0.05 μ. No bands near 9.1 μ were prominent. The three tertiary bisnitroso compounds examined did not show these bands, but did show bands of slightly uncertain significance near 7.85 μ. It was concluded that secondary bisnitroso compounds can be identified readily from their infrared spectra, but that no vibrational assignments for the bisnitroso group can be made yet.

Miscellaneous.—The spectra of five aliphatic ketoximes were examined in the liquid phase and found, as expected from previous work,[12] to be characterized by a strong O–H stretching band near 3.00 μ which became a sharp band near 2.8 μ in dilute solution, a weak to medium C═N stretching band at 6.0–6.1 μ, and a strong N–O stretching band at 10.3–10.8 μ. The last two bands were also seen in the spectra of the two oxime ethers which were examined.

Strong bands, probably due to N–O stretching, were observed in the spectra of two alkyl hydroxylamines near 11.5 μ. In hydroxylamine itself, the band comes at 11.18 μ.[13] In the hydroxylamines, the N–H stretching band appears at longer wave lengths than in the amines; for example, O,N-bis-(1-nitro-2-methyl-2-propyl)-hydroxylamine has showed a sharp unbonded N–H stretching band at 3.07 μ.

This investigation was little concerned with the nitrite esters or the azoxy compounds except to ascertain that they could be distinguished readily from the other types of compounds under consideration. Comparison of the positions of the strongest bands of cyclohexyl nitrite (6.10, 12.95 μ) with those of the isomeric nitrocyclohexane (6.46, 7.26 μ) or of cyclohexyl nitrate (6.15, 7.83, 11.49 μ) showed that there was little danger of confusion. The azoxy compounds are structurally and spectroscopically[14] very similar to the nitro compounds; however, none of the combinations of NO_2 asymmetrical and symmetrical stretching band positions observed in the various types of nitro compounds which we examined were very close to those reported for the azoxy compounds.

One final class of oxidized nitrogen compounds encountered in aliphatic nitration products are the furoxans. Spectra of such substances have been reported previously only for fused ring systems.[15] Our three monocyclic furoxans showed ring vibrations (C═N stretching?) near 6.15 and 6.36 μ. The 3-nitrofuroxans showed the expected bands of conjugated nitro groups at 6.64 and 7.36 μ.

Discussion

The Effects of Structural Variations on the NO_2 Stretching Bands in Nitro Compounds.—The preceding section has described a number of empirical correlations between the structures of nitro compounds and the position and intensity of the NO_2

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(9) F. Pristera, *Anal. Chem.*, **25**, 844 (1953).

(10) G. Ourisson, *Compt. rend.*, **230**, 1532 (1950).

(11) J. Goubeau and I. Fromme, *Z. anorg. Chem.*, **258**, 18 (1949).

(12) H. M. Randall, R. G. Fowler, N. Fuson and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand Co., Inc., New York, N. Y., 1949, p. 5; A. Palm and H. Werbin, *Can. J. Chem.*, **31**, 1004 (1953).

(13) P. A. Giguère and I. D. Liu, *ibid.*, **30**, 948 (1952).

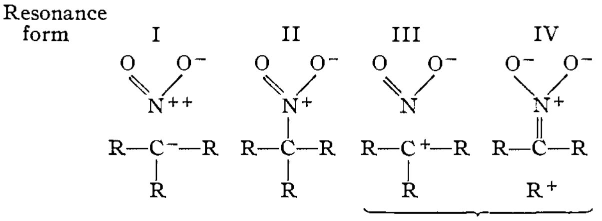
(14) B. W. Langley, B. Lythgoe and L. S. Rayner, *J. Chem. Soc.*, 4191 (1952).

(15) J. H. Boyer, D. I. McCane, W. J. McCarville and A. T. Tweedie, THIS JOURNAL, **75**, 5298 (1953).

stretching bands. Before further consideration of the analytical applications of these correlations, it seems highly desirable to establish the relationship of the correlations to more fundamental principles.

The effects of structural variations on the wave lengths of the NO_2 stretching bands in nitro compounds must result from variations in the mass, geometry and/or force constants of the vibrating system. However, the mass of an atom two or more atoms removed from those primarily involved in the vibrations cannot have much influence on its frequency, nor does it seem likely that the bond angles in the CNO_2 structure vary significantly in going from one type of nitro compound to another. Therefore, the observed variations in band position must be produced mainly by variations in the force constants of the C–N and N–O bonds. These, in turn, must result from variations in the bond orders (*i.e.*, the extent of unbonded, single bond or double character) of these bonds.

The bond orders corresponding to the principal types of resonance forms of an R_3CNO_2 structure (with no restriction on the nature of the R's) are indicated below.



Bond orders:		I	II	III, IV
	N–O	1.5	1.5	1.0–1.5[16]
	C–N	0	1.0	*ca.* 1

From these it may be seen that the replacement of, say, an α-hydrogen in a nitroalkane by a substituent R having a greater electron-donating ability should result in an increase in the contribution of forms III and IV over II, and hence result in a decrease in the N–O bond order. Conversely, a negative, or electron-attracting, substituent should favor the contribution of form I over II, III and IV, and hence result in some increase in the N–O bond order, along with a marked decrease in the C–N bond order.

The NO_2 asymmetric stretching vibration (Fig. 1) involves primarily stretching of the N–O bond and secondarily bending of the C–N bond. Since the C–N bond is of lower order then the N–O bond, and since bending force constants are much smaller than stretching force constants anyway, it may be concluded that the over-all force constant for this vibration will be very largely determined by the N–O stretching force constant, and hence the N–O bond order. Since, as we have seen, this in turn is determined by the electronic effects of the substituents on the CNO_2 group, we should expect a correlation between the wave length of the NO_2 asymmetric stretching band and the electron-donating ability of the structure to which the nitro group is attached.

The results are in accord with this expectation. Replacement of an α-chloro, nitro or acyl group by hydrogen, hydrogen by alkyl, or of an unconjugated by a conjugated structure causes the NO_2 asymmetric stretching band to shift to longer wave lengths (see Table II). The same shift also occurs in *m*- and *p*-substituted nitrobenzenes, as shown by the lower line on Fig. 2.

The NO_2 symmetric stretching vibration involves primarily stretching of the N–O bonds and secondarily stretching of the C–N bond (Fig. 1). Again, we may expect the over-all force constant to be determined mainly by the N–O stretching force constant. However, in this case we can no longer dismiss the effect of the C–N bond as negligible, since stretching rather than bending of the bond is involved. Accordingly, we should expect the effects of substituents on the NO_2 symmetric stretching frequency to parallel those on the asymmetric frequency only insofar as the C–N bond order is not disturbed. When electron-withdrawing substituents which reduce the C–N bond order are introduced, the NO_2 symmetrical stretching bond should appear at longer wave lengths than would otherwise be expected.

Observation supports this conclusion. The replacement of α-hydrogens by alkyl groups, or of unconjugated by conjugated structures does shift the NO_2 symmetrical stretching band, like the asymmetrical stretching band, to longer wave lengths, as shown by the solid lines in Fig. 3. On the other hand, the replacement of α-hydrogens or alkyls by chloro or nitro groups also causes the bond to shift to longer wave lengths, as shown by the dotted line in Fig. 3. The effect is also illustrated in Fig. 2 by the break in the upper plot which occurs when positive σ, *i.e.*, electron-withdrawing, substituents are introduced.

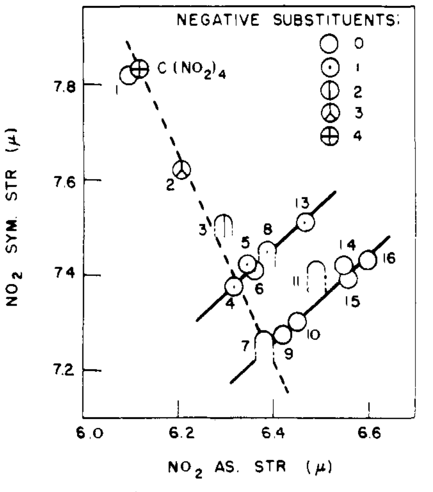


Fig. 3.—Relationship between positions of symmetrical and asymmetrical NO_2 stretching bands in nitro compounds. Numbers refer to compound type numbers in Table II. Average positions of the bands in polynitro compounds taken. Bottomless circles indicate true position of the NO_2 symmetrical stretching band uncertain because of possible interactions with methyl groups.

The intensities of infrared bands are determined by the magnitudes of the transition moments of the

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(16) We have considered only the aggregate effects of forms III and IV, since they are probably of comparable importance and both are similarly affected by structural variations.

vibrations which produce them. The transition moments are not readily calculated; however, we can say that any increase in charge separation in a vibrating system should be reflected by a corresponding increase in the band intensity of a vibration which occurs parallel to the direction of charge separation. In compounds where a nitro group is conjugated with an electron-releasing structure, resonance permits greatly increased charge separation. Hence, in such compounds we should expect the NO_2 symmetric stretching bands (vibration parallel to the direction of charge separation) to become stronger, while the NO_2 asymmetric stretching bands (vibration perpendicular to the charge separation) need not be affected. It was observed that the molar extinction coefficients of the NO_2 symmetrical stretching bands are roughly 100 for nitroalkanes, 300 for nitroalkenes, 600 for nitrobenzene and 1000 for *p*-nitroaniline; while the intensity of the asymmetric band seemed little affected by the type of structure to which the NO_2 group was attached.

The Use of Infrared Data in Structural Determinations.—The data have indicated that a variety of classes of organic oxidized nitrogen compounds and also a variety of types of structures containing nitro groups can be distinguished by their infrared spectra. The bands used for distinguishing between the different classes of compounds are sufficiently strong and distinct so that the identification of a particular class is generally unambiguous and reliable. More subtle distinctions are involved in differentiating between the various types of nitro compound structures, however, and in order to use such distinctions with confidence in structural determination work it is necessary to understand just what their potentialities and limitations are.

Infrared spectral data, like most other physical measurements, provide not a direct measurement of structure, but only of certain parameters related to it. The foregoing discussion has indicated that in the nitro compounds the structure-related parameters which can be directly determined from the infrared spectra are: (a) The electron-donating capacity of the structure attached to the nitro group (wave length of the NO_2 asymmetrical stretching band). (b) The presence of negative substituents on the α-carbon or the same unsaturated system as that attached to the nitro group (difference between the wave lengths of the NO_2 symmetrical and symmetrical stretching bands). (c) The extent of conjugation of the nitro group with the attached structure (relative intensities of the NO_2 symmetrical and asymmetrical stretching wave lengths). (d) The presence of structures having two or more nitro and/or methyl groups on the same carbon (splitting of the 7.3 μ band). (e) The presence of a negative group attached to a CH_2 (shift of the 6.9 μ band to 7.0 μ).

It follows that structures which differ from one another in any of the parameters a-e should be distinguishable *via* their infrared spectra, and the empirical classifications of structure type indicated by Table II and its accompanying discussion become possible.

There are a few practical limitations to the use of these distinctions. With regard to (b), the effects of the negative substituents on other than the α-carbon is probably too small to be used with confidence in structural determination. Occasionally, the bands involved in the distinctions (d) and (e) are difficult to identify because of overlapping with other bands. The precision of (c) appears to be such as to permit classification into only three categories: unconjugated (nitroalkanes), conjugated (nitroalkenes, most nitrobenzenes), and highly conjugated (*p*-nitroaniline, 2,4-dinitrophenylhydrazones). Incidentally, it may be noted that in such highly conjugated nitro compounds the usual recognition of the nitro group by a strong band in the 6.1–6.7 μ region is hindered by the fact that the NO_2 asymmetrical stretching band may be less prominent than other bands in the region; however, these compounds do have unusually strong NO_2 symmetrical stretching bands at 7.4–7.5 μ. The principal limitation to the use of (a) is the overlapping of the ranges of band positions in closely related types of structures. For example, Table II, which is based on measurements to ± 0.03 μ, indicates primary nitro alkanes as having bands at 6.39–6.45 μ, and secondary nitro alkanes at 6.43–6.47 μ. These ranges can be cut down somewhat by making measurements to ± 0.01 μ, but an observed wave length of 6.44 μ would still be inconclusive. In such a case, in order to be certain as to whether the compound in hand was primary or secondary, recourse would have to be made to either the position of the symmetrical stretching band, which would be even more likely to be inconclusive, or to the distinction (e).

Despite these minor limitations, it is still possible to distinguish among, and reliably identify, many different types of structures containing nitro groups. During structural determinations on several dozen new nitro compounds, our experience indicated that the infrared correlations in no case led to incorrect, and only rarely to ambiguous structural conclusions.

Benzene Ring Vibrations.—The band near 6.7 μ in the nitrobenzenes corresponds to the ν_{13} (Herzberg's notation[17]) vibration in benzene itself, and may be described as a C–C stretching vibration. The unexpected correlation between the wave length of this band and the Hammett σ constant of the substituent was of great interest in that it suggested a means of determining relative bond orders in benzene rings from spectral data. There are, however, two factors which may somewhat limit such determinations. First, it is not certain to what extent the band position may be affected by the mass and orientation of the substituent, although the fact that any correlation with σ was observed at all does show that these effects must be less important than the electronic effects. Second, while the ν_{13} vibration in benzene itself corresponds to a twofold degenerate C–C stretching mode, the degeneracy is released in the substituted benzenes. In our substituted nitrobenzenes there should be two vibrations, which might or might not correspond to distinct and recognizable

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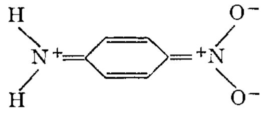
(17) G. Herzberg, "Infrared and Raman Spectra," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 362.

spectral bands. Accordingly, we cannot be certain that the observed band near 6.7 μ corresponds to quite the same stretching mode in all cases.

One conclusion does seem possible, however. The 6.6–6.7 μ band in compounds like *p*-nitroaniline, *p*-nitrophenol and *p*-nitroanisole must correspond to C–C stretching parallel to the main axis of the molecule. This is indicated by the great intensity of the band in these compounds, which suggests vibration parallel to the dipole, and the fact that no interaction occurs between this vibration and the NO_2 asymmetrical stretching vibration, even when the frequencies coincide, as they do in *p*-nitroaniline (see Fig. 2). The shift of the band to shorter wave lengths by substituents having more negative σ-values indicates an increase in the order of the bonds parallel to the molecular axis, and is in accord with the view that resonance forms such as V are contributing to the over-all structure of these molecules.



V

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SCHENECTADY, N. Y.

[CONTRIBUTION FROM THE BOTANY DEPARTMENT, CORNELL UNIVERSITY]

The Identification of Compound A from Coconut Milk as 1,3-Diphenylurea[1]

BY E. M. SHANTZ AND F. C. STEWARD

RECEIVED MAY 7, 1955

Compound A from coconut milk has been reisolated and identified as 1,3-diphenylurea, identical with a synthetic sample in its physical, chemical, and biological properties. In combination with casein hydrolysate, it promotes growth by cell division in cultures of carrot phloem tissue in a manner similar to coconut milk but to a lesser extent. The degree of response is variable, being dependent upon inherent characteristics of the individual carrot root from which the explants are taken. The chemical determination of the probable maximum level of anilide in a different sample of coconut milk is also reported.

In the attempt to determine the chemical nature of the substances in coconut milk responsible for the stimulation of growth in mature carrot phloem cells, Shantz and Steward[2] described the isolation and general characteristics of three crystalline compounds, then designated as A, B and C. Compound A has now been reisolated in larger amount and identified as 1,3-diphenylurea, identical in both chemical and biological properties with a synthetic sample.

The first small isolate of compound A was obtained as a crude crystalline product when an alcoholic extract of the mercury-freed precipitate from approximately 700 gallons of coconut milk, that had been treated in 50% alcohol with mercuric acetate, was concentrated and filtered. The second isolation of compound A in larger amount was made from the neutral fraction of the ether extract from the above filtrate. This fraction (72 g.) was dissolved in 500 ml. of petroleum ether (b.p. 60–70°) and seeded with a fraction of a mg. of compound A crystals previously obtained. The solution was filtered after storage at room temperature for 7 days, leaving a residue of 480 mg. of light brown needles. No further crystalline material could be obtained even after concentration to 200 ml. and prolonged storage at 5°. The crude crystalline product was recrystallized three times from hot absolute ethanol to give a final yield of 317 mg. of fine white needles.

Analyses[3] on the isolated product gave: C, 73.58; H, 5.78; O, 7.63; N, 13.17; mol. wt. between 173 and 230 as determined by isothermal distillation with acetone. Required for $C_{13}H_{12}N_2O$: C, 73.57, H, 5.70, O, 7.54; N, 13.19; mol. wt., 212. The melting points of the isolated compound A (241–243.5°) and synthetic 1,3-diphenylurea (242–244.5°) showed no depression on mixing (242–244°). Complete infrared scans (potassium bromide disc method) of the natural compound A and synthetic 1,3-diphenylurea were identical, as were the ultraviolet absorption spectra in methanol and in ethanol.

The ability of compound A to induce growth in carrot explants was originally tested by methods adopted in this Laboratory[4] using explants from a number of different roots. Although the magnitude of the growth response was to a large extent a function of the individual carrot roots, activity was demonstrated in most of the experiments carried out at that time.[5] The addition of compound A at about 1 p.p.m. to the basal medium had but little effect on growth, but if casein hydrolysate were also added, the growth response frequently approached that obtained by the addition of whole coconut milk. The criterion of growth in these experiments was the increase in fresh weight shown by the cultured explants. By maceration and cell counting techniques, to be described elsewhere, it is now pos-

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(2) E. M. Shantz and F. C. Steward, THIS JOURNAL, **74**, 6133 (1952).

(3) The authors gratefully acknowledge the assistance of Drs. R. H. Wallick, J. J. Kirkland, R. L. Dalton, and other members of the Technical Division of the Grasselli Chemicals Department of E. I. du Pont de Nemours & Company in obtaining the analytical data.

(4) F. C. Steward, S. M. Caplin and F. K. Millar, ***Ann. Bot.*** *N.S.*, **16**, 57 (1952).

(5) F. C. Steward and E. M. Shantz, ***Année Biol.***, **30**, 399 (1954).