methanol-chloroform (5 ml. each) were made. Cooling was necessary to control the exothermic reaction after each addition. The additions took 2 hr. Heating under reflux was continued for 5 min. and the organic solvents were removed under reduced pressure. The solid residue was dissolved in water (1100 ml.), and ether (500 ml.) and 3% hydrochloric acid were added until the aqueous phase was acid to Congo Red, with vigorous stirring and ice-cooling. The ether extract was dried (sodium sulfate), the solvent was removed, and the residue was recrystallized from benzene-pentane; yield, 34%. The cream-colored solid darkened on heating but showed no definite m.p. below 300°. It was, however, pure and showed strong absorption in the infrared at 4.70 μ corresponding to the $-N{\equiv}C$ group.

Anal. Calc'd for $C_8H_5NO_2$: C, 65.30; H, 3.43; N, 9.52; Neut. equiv., 147. Found: C, 65.08; H, 3.76; N, 9.26; Neut. equiv., 162.

p-Isocyanobenzenesulfonamide. To a refluxing mixture of *p*-aminobenzenesulfonamide (17.2 g.), sodium hydroxide (20 g.), and ether (50 ml.), was added dropwise with stirring a mixture of chloroform (28 ml.) and ethanol (5 ml.). The exothermic reaction maintained the mixture at the reflux. After the addition was complete (1 hr.), refluxing was continued for 15 min. The solvents were removed under reduced pressure and the solid residue was extracted with ethyl acetate in a Soxhlet extractor during 24 hr. After removal of the ethyl acetate, the cream-colored product was recrystallized from benzene, m.p. 235–237° (some softening at 120°); yield, 5%. Infrared absorption of $-N{\equiv}C$ group at 4.71 μ.

Anal. Calc'd for $C_7H_6N_2O_2S$: C, 50.60; H, 3.64; N, 16.86; S, 19.27. Found: C, 50.94; H, 3.26; N, 16.42; S, 19.66.

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The Infrared Absorption Spectra of Nitroparaffins and Alkyl Nitrates[1,2]

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In the course of studying the chemistry of nitroparaffins and alkyl nitrates the infrared spectra of a large number of compounds have been determined. This paper summarizes and discusses our data.

Nitroparaffins. While four bands have been ascribed to the aliphatic nitro group a definitive assignment has yet to be made (*cf.* Table I).[3] The present investigation shows that the band in the 4.00–4.17 μ region is a very weak one, without value for diagnostic purposes.

TABLE I

INFRARED ABSORPTION BANDS PREVIOUSLY ASCRIBED TO THE ALIPHATIC NITRO GROUP

Wave Length (μ)				Ref.
4.00–4.17	6.29–6.49	7.25–7.58		*a*
	6.35–6.65	7.30–7.65		*b*
	6.4	7.4	11.75	*c*
	6.37–6.42	7.25–7.35	10.90–12.4	*d*
	6.38–6.45	7.24–7.38	10.90–11.97	*e*
	6.23–6.56	7.2–7.6		*f*

[a] Miller in Gilman's *Organic Chemistry*, Vol. III, p. 149, 1953, John Wiley and Sons, New York, N. Y. [b] Colthup, *J. Opt. Soc. Amer.*, **40**, 397 (1950). [c] Shechter and Conrad, *J. Am. Chem. Soc.*, **76**, 2717 (1954). [d] Smith, Fan and Nielsen, *J. Chem. Phys.*, **18**, 707 (1950). [e] Haszeldine, *J. Chem. Soc.* 2526 (1953). [f] Randall, Fowler, Fuson, and Dangl, *Infrared Determination of Organic Structures*, p. 20, D. Van Nostrand Company, New York, N. Y., 1949.

While all previous workers have agreed that absorption characteristic of the aliphatic nitro group occurs in the 6.4 μ region there has been no way of telling just where to expect this band. It is now clear that primary and secondary nitro compounds absorb at 6.45 ± 0.01 μ and that tertiary nitroparaffins absorb at 6.51 ± 0.01 μ (Table II). In α-nitroesters this band is displaced to shorter wavelengths by *ca.* 0.05 μ. The striking regularity with which the band in the 6.4 μ region is found, plus the fact that it is unusually strong, renders it by far the most valuable infrared characteristic of aliphatic and alicyclic nitro compounds.[4]

Identification of the nitro band in the 7 μ region has been rather uncertain because of its proximity to a band associated with the methyl group. As a consequence previous assignments have been somewhat arbitrary. The data of Table II show that the band at 7.25 ± 0.02 μ is characteristic of primary nitro compounds for it is found regardless of whether or not a methyl group is present. Indeed, this is the only strong absorption band in the 7 to 7.5 μ region.

With secondary nitroparaffins band allocation in the 7 μ region is complicated by the occurrence of several bands in the 7 to 7.5 μ region. In the case of 2-nitropropane absorption maxima are found at 7.16, 7.30, and 7.37 μ. It is assumed that the peaks at 7.16 and 7.30 μ are due to the methyl groups of the isopropyl part of the molecule since such splitting is known to occur in isopropyl systems.[5] This leaves the band at 7.37 μ to be assigned to the nitro group. With 2-nitrobutane, and higher secondary open-chain nitro compounds, only two bands are observed in the 7.0 to 7.5 μ region. The one of longer wave length has arbitrarily been identified with the nitro group.[4] Although the methyl and nitro bands in this region are generally well separated, they are

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[1] Paper XIV in the series "The Chemistry of Aliphatic and Alicyclic Nitro Compounds."

[2] This research was supported by the United States Air Force under Contract No. AF 18 (600)-310 monitored by the Office of Scientific Research, Air Research and Development Command.

[3] See also, L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, N. Y., 1954, pp. 250–251. Note the important paper by J. F. Brown which appeared after our work was completed [*J. Am. Chem. Soc.*, **77**, 6341 (1955)].

[4] This conclusion was previously reached by Smith, Fan, and Nielsen on the basis of much more limited evidence [*J. Chem. Phys.*, **18**, 707 (1950)].

[5] Foil Miller in Gilman's *Organic Chemistry*, Vol. III, p. 143, 1953, John Wiley and Sons, New York, N. Y.

TABLE II

INFRARED ABSORPTION SPECTRA OF ALIPHATIC NITRO COMPOUNDS

Compound	Absorption Bands, μ	
1-Nitrobutane	6.45	7.25
1-Nitropentane	6.45	7.25
1-Nitrohexane	6.45	7.25
1-Nitroheptane	6.44	7.25
1-Nitrooctane	6.45	7.25
1-Nitrodecane	6.45	7.25
2-Methyl-1-nitropropane	6.46	7.25
3-Methyl-1-nitrobutane	6.45	7.24
Cyclohexylnitromethane	6.44	7.23
Phenylnitromethane	6.44	7.27
2-Phenyl-1-nitroethane	6.44	7.25
3-Phenyl-1-nitropropane	6.45	7.24
Ethyl nitroacetate	6.39	7.29
2-Nitropropane	6.44	7.37
2-Nitrobutane	6.46	7.36
2-Nitroheptane	6.46	7.37
3-Nitroheptane	6.46	7.30
4-Nitroheptane	6.45	7.37
2-Nitrooctane	6.46	7.37
2-Nitro-5-methyloctane	6.46	7.33
Nitrocyclopentane	6.47	7.30
Nitrocyclohexane	6.45	7.25
1-Phenyl-2-nitropropane	6.46	7.35
Ethyl α-nitropropionate	6.40	7.35
Ethyl α-nitrobutyrate	6.41	7.31
Ethyl α-nitroisovalerate	6.40	7.30
Ethyl α-nitrocaproate	6.40	7.32
Ethyl α-nitro-α-phenylacetate	6.38	7.35
2-Methyl-2-nitropropane	6.50	7.44
2-Methyl-2-nitrobutane	6.52	7.40
2-Methyl-2-nitrooctane	6.51	7.41
2,4-Dimethyl-2-nitropentane	6.51	7.44
2,2,4-Trimethyl-4-nitropentane	6.50	7.40
1-Methyl-1-nitrocyclopentane	6.51	7.41
1-Methyl-1-nitrocyclohexane	6.51	7.45
Ethyl α-nitroisobutyrate	6.44	7.40

fused in a number of instances, one band appearing as a shoulder on the other; sometimes the methyl band is the shoulder, sometimes the nitro band. Nitrocyclopentane and nitrocyclohexane are, of course, free of complications due to methyl. The former has only one peak between 7.0 and 7.5 μ (at 7.30 μ) and this is assigned to the nitro group. In addition, there is a band at 7.56 μ which is, presumably, due to the cyclopentane system for cyclopentane itself absorbs near 7.6 μ.[6] Nitrocyclohexane has two bands, a strong one at 7.25 μ which is assigned to the nitro group, and a weaker one at 7.39 μ which corresponds to the known cyclohexane band at 7.41 μ.[6]

tert-Nitrobutane (2-methyl-2-nitropropane) shows three well defined absorption bands in the 7.0 to 7.5 μ region: 7.14, 7.30, 7.44 μ. We assume that the 7.14 and 7.30 μ bands are due to the *tert*-butyl group[5] (an assumption which is supported by the fact that the 7.30 μ band is the stronger one) and allocate the band at 7.44 μ to the nitro group. The other open chain tertiary nitro compounds examined also have three distinct absorption maxima: 2-methyl-2-nitrobutane (7.16, 7.30, and 7.40 μ); 2,4-dimethyl-2-nitropentane (7.17, 7.31, and 7.44 μ); 2-methyl-2-nitrooctane (7.16, 7.29, and 7.41 μ); 2,2,4-trimethyl-4-nitropentane (7.13, 7.28, and 7.40 μ); ethyl-α-nitroisobutyrate (7.14, 7.29, and 7.40 μ). For reasons given above, the band of longest wave length is, in each case, assigned to the nitro group.

In complete conformity with the fact that they do not possess *gem* dimethyl groups, 1-methyl-1-nitrocyclopentane and 1-methyl-1-nitrocyclohexane each have only two bands in this region, the former compound at 7.24 and 7.41 μ and the latter at 7.22 and 7.45 μ. As before,[4] the band of longer wave length is identified with the nitro group.

One cannot help contrasting the complexities attending assignment of the nitro absorption characteristic in the 7 μ region with the very great ease of identifying nitro absorption in the 6.4 μ region. The 7 μ band can only be regarded as possessing auxiliary importance for identification purposes.

Finally, it will be seen from Table I that several writers have assigned a band to the nitro group in the neighborhood of 11 μ. Inspection of the absorption curves of the compounds listed in Table II reveals that while there is a band in this region it is often rather weak and it shows no regularity in regard to wave length. Consequently, the 11 μ band does not appear to be of value as a diagnostic for the nitro group.

Nitrate esters. The infrared spectra of nitrate esters are characterized by two sharp, intense, absorption bands close to 6.14 and 7.84 μ and a third, also intense, but broad band centered around 11.5–11.7 μ (Table III). These results are in agreement with the rather limited data available.[7]

TABLE III

INFRARED ABSORPTION SPECTRA OF NITRATE ESTERS

Nitrate	Absorption Bands (μ)		
Methyl[a]	6.12	7.80	11.6
1-Octyl	6.14	7.84	11.6
Cyclopentylmethyl	6.13	7.83	11.6
Cyclohexylmethyl	6.14	7.83	11.5
2-Butyl	6.15	7.86	11.6
4-Heptyl	6.15	7.84	11.5
2-Octyl	6.15	7.84	11.6
5-Methyl-2-octyl	6.15	7.84	11.6
α-Phenylethyl	6.14	7.83	11.7

[a] Reported by Brand and Cawthon (ref. 7).

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(6) *Catalog of Infrared Spectrograms,* American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa.

(7) *cf.* Ref. 3. Also see J. Lecomte and J. P. Mathieu, *J. Chim. phys.,* **39,** 57 (1942); R. Boschan, R. T. Merrow, and R. W. Van Dolah, *Chem. Revs.,* **55,** 490 (1955); J. Levy, *J. Am. Chem. Soc.,* **76,** 3254 (1954), has employed the peak at 11.73 μ in analyzing for ethyl nitrate. Recently a very careful study of the infrared spectrum of methyl nitrate has been reported by J. C. D. Brand and T. M. Cawthon, *J. Am. Chem. Soc.,* **77,** 319 (1955); *cf.* Table III.

EXPERIMENTAL

The preparation and properties of the nitro compounds, α-nitroesters, and nitrate esters have been described previously.[8]

The infrared absorption spectra were determined with a Perkin Elmer Model 21 spectrophotometer. In all cases the pure liquid was employed.

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Preparation of *o,o'*-Dihydroxyazo Compounds[1,2]

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A number of *o,o'*-dihydroxyazo compounds were desired in an investigation of the fluorescence of metal chelates. Some of these could not be made by standard coupling procedures because of unfavorable directing influences. A new procedure for the preparation of symmetrical azo compounds has been published by Bogoslovskii,[4] but he did not report the preparation of any compounds containing *o*-hydroxy groups. When Bogoslovskii's procedure was used for the preparation of *o*-hydroxyazo compounds the product was found to be isolable as the stable copper chelate. The compounds prepared and the procedures used are detailed below.

EXPERIMENTAL

2,2'-Dihydroxyazobenzene (I). The catalyst stock solution was prepared as follows: Copper(II) sulfate pentahydrate (28.5 g.) was dissolved in 100 ml. of hot water. The solution was cooled and treated with concentrated ammonium hydroxide until the formation of the soluble ammonia complex was complete. This was reduced to the colorless copper(I) solution with 7 g. of hydroxylamine hydrochloride in 20 ml. of water just before use.

For the preparation of the diazonium mixture concentrated hydrochloric acid was added dropwise to 250 ml. of a solution of 11.0 g. of *o*-aminophenol and 7.0 g. of sodium nitrite in 5% sodium hydroxide until a positive reaction was observed with starch-iodide paper. The temperature was kept below 10° during this reaction. The diazonium mixture was added rapidly to the catalyst solution which was stirred constantly. Excessive foaming was prevented with ether. The mixture was allowed to stand for about one hour, stirred occasionally, and then was collected on a filter. The brown copper chelate isolated was found to be identical with that of Drew and Landquist.[5] This chelate was mixed with 500 ml. of concentrated hydrochloric acid and warmed gently. The mixture then was diluted with an equal volume of ice-water and filtered. The product was recrystallized three times from benzene to give a 53% yield of yellow-orange needles which melted at 172–172.7° (Lit.[6] 172°). The yield was increased to 78% by continuous liquid-liquid extraction of the diluted hydrochloric acid mixture with ether.

Anal. Calc'd for $C_{12}H_{10}N_2O_2$: C, 67.3; H, 4.71; N, 13.08. Found: C, 67.17; H, 4.54; N, 13.40.

2,2'-Dihydroxy-5,5'-dimethylazobenzene (II). 2-Nitro-4-methylphenol was prepared by the method of Neunhoeffer and Kolbel.[7] This was reduced to the amine in 69% yield by hydrogenation in dioxane with Raney nickel at room temperature. The copper chelate of II was prepared in the same manner as that of I. A solution of 5.5 g. of the chelate in 100 ml. of commercial ether was treated with hydrogen sulfide for 15 minutes. The mixture was filtered with Celite to remove the copper(II) sulfide and the ether was removed by evaporation. The product was recrystallized from petroleum ether (60–80°) with Norit to give a 28% yield of yellow needles, m.p. 219–220°.

Anal. Calc'd for $C_{14}H_{14}N_2O_2$: C, 69.5; H, 5.82; N, 11.56. Found: C, 69.34; H, 6.00; N, 11.60.

2,2'-Dihydroxy-4,4'-dimethylazobenzene (III). 2-Nitro-5-methylphenol was prepared by the method of Staedel,[8] and reduced to the amine as by Proskouriakoff and Titherington.[9] The copper chelate of III was prepared in the same manner as that of I. A concentrated hydrochloric acid solution of 10.0 g. of the chelate was boiled gently for about 10 minutes. The product separated as a black oily mass on top of the deeply colored hydrochloric acid. The mixture was cooled, and after 200 ml. of ice-water was added it was filtered with Celite. The dried mass then was extracted with benzene in a Soxhlet extractor. The product was crystallized from the extract and then from petroleum ether (90–100°) to give a 40% yield of bright yellow needles, m.p. 223–224°.

Anal. Calc'd for $C_{14}H_{14}N_2O_2$: C, 69.5; H, 5.82; N, 11.56. Found: C, 69.64; H, 5.93; N, 11.92.

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[2] Supported in part by a grant from Arthur D. Little, Inc.

[3] Present address: Linde Air Products Co., Tonawanda, N. Y.

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