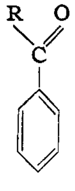
[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, ILLINOIS INSTITUTE OF TECHNOLOGY]

Raman Spectra Evidence for Hindrance of Resonance by Ortho Substitution

BY ROBERT H. SAUNDERS, M. J. MURRAY AND FORREST F. CLEVELAND

In 1937 Birtles and Hampson[1] showed, by comparing dipole moments, the effectiveness of ortho methyl groups in minimizing the contributions of certain resonating forms in nitrodurene and related compounds. O'Shaughnessy and Rodebush[2] have shown by means of ultraviolet absorption that such effects also exist in certain substituted acetophenones. Kadesch and Weller[3] have obtained dipole moments of acetylmesitylene, mesitylaldehyde, 2,4,6-trimethylbenzoyl chloride, and acetyldurene; and by comparison with the dipole moments of the corresponding phenyl and aliphatic derivatives have observed similar steric hindrance effects in all of the above compounds except mesitylaldehyde.

Such steric effects should also be observable in Raman spectra. The information that can be obtained from the Raman spectra concerns the forces between atoms in a molecule in its normal state, the arrangement of the atoms, and the character of the vibrations. Therefore, the twisting effect caused by the introduction of ortho methyl groups into a planar molecule such as acetophenone should change the frequencies of some of the characteristic Raman lines. In aromatic carbonyl compounds the ortho substitution of two methyl groups decreases the contributions of forms II and III to the normal state of the molecule[3] and should effect a change in the $C{=}O$ frequency. Likewise, the introduction of two ortho methyl groups into nitrobenzene decreases the contributions of forms V and VI[1,4] and should change the symmetrical valence vibrations of the oxygen atoms in the nitro group. To determine whether or not the above changes were large enough to be significant, acetyldurene, nitromesitylene, and several carbonyl derivatives of mesitylene were examined by means of the Raman effect. Since only the carbonyl and nitro frequencies are of interest in the present discussion, a more complete consideration of the Raman spectra of these compounds is reserved for a future communication.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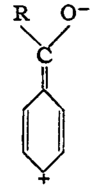
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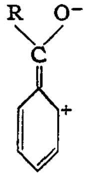
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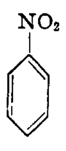
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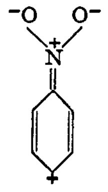
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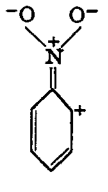
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Experimental

Preparation of Materials

All of the following compounds except acetyldurene were fractionated at reduced pressure through a heated column of modified Podbielniak type, thirty centimeters long.

Acetophenone.—B. p. 98.5° at 25 mm. **Acetylmesitylene** from mesitylene and acetic anhydride with anhydrous aluminum chloride: b. p. 123.5–124.5° at 19 mm. **Acetyldurene** from durene and acetic anhydride and purified by repeated recrystallization from ether: m. p. 74.0°. **Mesitylaldehyde** from mesitylene, hydrogen chloride, and carbon monoxide, with cuprous chloride: b. p. 107–108° at 8–9 mm.

2,4,6-Trimethylbenzoyl Chloride.—2,4,6-Trimethylbenzoic acid, prepared from bromomesitylene by a Grignard reaction, was treated with thionyl chloride and the product collected 118–119° at 19 mm. **Methyl 2,4,6-trimethylbenzoate** from the acid chloride with anhydrous methanol: b. p. 102–103° at 5.5 mm. **Nitromesitylene** by nitration of mesitylene with fuming nitric acid in acetic anhydride; pale yellow crystals, b. p. 104–106° at 6 mm.

Raman Spectra

The apparatus and experimental technique used in obtaining the Raman spectra are described elsewhere.[5] Hg 4358 Å. was used for excitation. Exposures were about three and one-half hours with a slit width of 0.08 mm. The spectrum of acetyldurene was obtained in carbon tetrachloride solution. Nitromesitylene was kept liquid during the exposure by an electric heating element wound around the Raman tube. Most of the exciting light was absorbed by nitromesitylene and Raman lines could be obtained only on long exposures.

Discussion

The Raman frequencies of carbonyl groups are notably lowered by conjugation with an aromatic

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[1] Birtles and Hampson, *J. Chem. Soc.*, 10 (1937).

[2] O'Shaughnessy and Rodebush, THIS JOURNAL, **62**, 2906 (1940).

[3] Kadesch and Weller, *ibid.*, **63**, 1310 (1941).

[4] Ingham and Hampson, *J. Chem. Soc.*, 981 (1939).

[5] Cleveland, Murray, Haney and Shackelford, *J. Chem. Phys.*, **8**, 153 (1940); Cleveland and Murray, *ibid.*, **7**, 396 (1939).

radical. However, if the aromatic group is removed from the carbonyl by one or more carbons, there is no longer a significant interaction between them, and the carbonyl frequency becomes very close to its value in aliphatic compounds. Thus the carbonyl shift in benzaldehyde at 1700 cm.$^{-1}$ is increased to 1718 cm.$^{-1}$ when a CH_2 group separates the carbonyl and the ring (*i. e.*, phenylacetaldehyde). This same effect is found in the case of ketones, esters, and acid chlorides. The effect of centralization of mass at the alpha carbon atom appears to be small in comparison with the conjugation effect. Thus the carbonyl shift for aldehydes and ketones changes about eight wave numbers when the alpha carbon atom changes from a primary to a tertiary group, while conjugation lowers the carbonyl frequency twenty to thirty wave numbers. The frequency shift for the nitro group also changes considerably when conjugated with an aryl group. In aliphatic nitro compounds the frequency characteristic of the nitro group is found around 1367 cm.$^{-1}$, while in nitrobenzene the interaction of the nitro with the ring causes the frequency to drop to 1341 cm.$^{-1}$.

In Table I the carbonyl frequencies of compounds of the type $R\overset{\overset{O}{\|}}{C}X$ (where R = benzyl, phenyl, *o*-tolyl, mesityl and duryl, and X = CH_3, H, Cl, and OCH_3) are compared. The frequencies of the nitro group in nitrobenzene and nitromesitylene are included. The benzyl derivatives show the effect of eliminating resonance by separating the two groups. The phenyl derivatives, on the other hand, show the effect of complete resonance between the ring and carbonyl. The mesityl derivatives show how resonance is eliminated by the steric effects of the two ortho methyl groups.

TABLE I

RAMAN SHIFTS FOR CARBONYL AND NITRO GROUPS IN CONJUGATED AND UNCONJUGATED SYSTEMS

		Frequencies in cm.$^{-1}$						
	X R...	Benzyl	Phenyl		*o*-Tolyl		Mesityl	Duryl
$R\overset{\overset{O}{\|}}{C}X$	CH_3	1697[a]	1684[g]		..		1699[g]	1699[g]
	H	1718[a]	1700[g]		1688[f]		1687[g]	..
	Cl	1797[a]	1727	1768[a]	1725	1770[e]	1792[g]	..
	OCH_3	1732[a]	1718[b]		1716[b]		1728[g]	..
RX	NO_2	1367[c]	1341[d]		1345[c]		1363[g]	..

[a] Kohlrausch and Pongratz, *Sitzber. Akad. Wiss. Wien*, Abt. IIb, **143**, 288 (1934). [b] *Ibid.*, **142**, 637 (1932). [c] Dadieu, Jele and Kohlrausch, *ibid.*, IIa, **140**, 293 (1931). [d] Dadieu and Kohlrausch, *Physik. Z.*, **31**, 514 (1930). [e] Kohlrausch, Pongratz and Stockmair, *Sitzber. Akad. Wiss. Wien*, Abt. IIb, **144**, 678 (1935). [f] Bonino and Manzoni-Ansidei, *Mem. R. Accad. Scienze Ist. Bologna, Classe di Scienze Fisiche*, [9] **1**, 27 (1933–1934). [g] Present results.

From Table I it can be seen that the carbonyl shifts for acetophenone, benzoyl chloride, and methyl benzoate have been increased by the introduction of two ortho methyl groups. The carbonyl values for these ortho-substituted derivatives (*i. e.*, acetyldurene and the mesityl compounds) are almost the same as the values found for the corresponding benzyl compounds. This would indicate that resonance between the ring and carbonyl group had practically ceased, and show that two ortho methyl groups are nearly as effective as an intervening CH_2 group for the elimination of conjugation in such compounds. This increase in carbonyl shift in acetyldurene, acetylmesitylene, 2,4,6-trimethylbenzoyl chloride, and methyl 2,4,6-trimethylbenzoate is brought about by the steric effect of the ortho methyls. These ortho groups are large enough to prevent the planarity of the molecule[1,2,3,4] which is indispensable for the conjugation of the ring and carbonyl group.

A similar effect is noted in the case of nitro compounds. The nitrobenzene value of 1341 cm.$^{-1}$ is increased to 1363 cm.$^{-1}$ in nitromesitylene, which is only a few wave numbers below the value of 1367 cm.$^{-1}$ for an unconjugated nitro group.

The carbonyl frequency in benzaldehyde, on the other hand, shows no increase upon the introduction of ortho methyl groups; instead, the carbonyl frequency of mesitylaldehyde actually drops twelve wave numbers below the value for benzaldehyde. This lowering seems to be too great to be attributed solely to the mass effect of the added methyl groups, especially since *o*-tolylaldehyde, which contains only one ortho methyl group, has practically the same shift as mesitylaldehyde. The function of the methyl groups in this case may concern not their size but their inductive properties. The aldehyde group is small enough to lie in the plane of the ring despite the ortho methyls,[3] so, instead of hindering resonance by inhibiting coplanarity, the methyl groups may actually enhance the resonance of the ring with the carbonyl group by induction at the ortho and para positions. In this way there would be a stabilization of the resonating quinoid structures II and III in contrast with the case of acetylmesitylene where these forms are almost completely eliminated. This inductance is not apparent for the mesityl ketone, acid chloride or ester, probably because the size of these groups does not allow the complete coplanarity necessary to take full advantage of these effects.

Both the dipole moment and Raman data are consistent in showing values for acetyldurene, acetylmesitylene, 2,4,6-trimethylbenzoyl chloride and nitromesitylene, that are intermediate between the values for the corresponding aromatic and aliphatic compounds.

Summary

It has been shown that the steric effects of ortho methyl groups in nitromesitylene and mesitylenic carbonyl derivatives may be detected readily in the Raman spectra of these compounds. The frequencies of the carbonyl and nitro groups in the above compounds approach the values found for unconjugated derivatives. This indicates that resonance between the ring and carbonyl or nitro group is greatly reduced. These conclusions are consistent with those drawn from dipole moment data for the same compounds.

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[CONTRIBUTION FROM THE HAYDEN MEMORIAL LABORATORIES, NORTHEASTERN UNIVERSITY]

Ammonium Salts of Aliphatic Carboxylic Acids

BY SAVERIO ZUFFANTI

A review of the literature indicates that very few of the ammonium salts of aliphatic carboxylic acids have been prepared in the anhydrous state. Ammonium formate (m. p. 116–117°) has been prepared by Groschuff,[1] and also by Kendall and Adler.[2] Davidson and McAllister[3] prepared ammonium acetate (m. p. 113–114°) by introducing dry ammonia gas into a desiccator containing anhydrous acetic acid in a small evaporating dish placed over soda-lime. The ammonia in the salts thus prepared was always found to check the theoretical value to within a few tenths of one per cent.

Ammonium propionate has been prepared but no constants are reported. Reik[4] states that, on vacuum distillation, this salt melts with brisk evolution of ammonia and leaves a residue of propionic acid. No information is available on any of the other ammonium salts of aliphatic carboxylic acids.

These salts are very hygroscopic, *i. e.*, anhydrous ammonium propionate (reported in this paper) has a melting point of 107°, but short contact with the atmosphere caused it to gain water resulting in a product that melts at 45°.

The purpose of this paper is to describe a method of preparing the anhydrous salts and also obtaining their melting points without the necessity of transferring the products and allowing contact with atmospheric moisture. Keeping the salts in an atmosphere of ammonia, during the melting point determination, also decreases the tendency of the salts to decompose into mixtures of salt and free acid which would have varying melting points.[3]

Experimental

Materials.—Formic and acetic acids were made anhydrous by the methods of Kendall and Gross.[5] All the other acids used were purchased from Eastman Kodak Co. and were made anhydrous by fractional crystallization and distillation under anhydrous conditions until the proper freezing points were obtained.[6]

Apparatus.—The apparatus consists of three 10-cm. U-tubes connected in series. The center U-tube is used as the reaction chamber, while the other two U-tubes are filled with barium oxide and serve as drying tubes. The end U-tube is connected to a bubbler, containing a few cubic centimeters of concentrated ammonium hydroxide, which serves to indicate the rate of flow of the ammonia gas. The center U-tube is immersed in a glycerol-bath to obtain uniform heating. Two thermometers are used to obtain the temperature inside (t^1) and outside (t^2) of the reaction chamber.

Preparation of the Anhydrous Ammonium Salts.—Ammonia gas is allowed to sweep out the system for approximately fifteen minutes. A small amount (about 0.5 cc.) of the anhydrous carboxylic acid is sprayed down the wall of the center U-tube using a medicine dropper with a restricted opening. A thin layer of white crystals of the ammonium salt immediately forms on the wall of the U-tube. The flow of gas is continued at the rate of approximately one bubble per second for a half hour or until the reaction appears to be complete, before starting the melting

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[1] Groschuff, *Ber.*, **36**, 1783 (1903).

[2] Kendall and Adler, THIS JOURNAL, **43**, 1473 (1921).

[3] Davidson and McAllister, *ibid.*, **52**, 507 (1930).

[4] Reik, *Monatsh.*, **23**, 1053 (1902).

[5] Kendall and Gross, THIS JOURNAL **43**, 1431 (1921).

[6] Belcher, *ibid.*, **60**, 2744 (1938).