[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS,
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THE INFRARED SPECTRA OF CHELATE COMPOUNDS. I. A STUDY OF THE CARBONYL FREQUENCIES OF THE HYDROGEN AND METAL CHELATES OF THE SUBSTITUTED CYCLOHEPTATRIENONES

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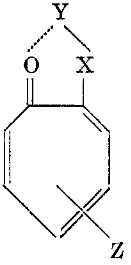
Received May 25, 1954

INTRODUCTION

Infrared absorption spectroscopy has rapidly assumed a position of eminence in structural studies, not only because the positions of characteristic peaks can be assigned to definite linkages, but also because shifts of these peaks can be related to the interaction of two or more functional groups. Several publications (1–7) have called attention to the marked shift towards longer wave lengths in the carbonyl frequencies of compounds in which internal hydrogen-bonding (chelate ring formation) occurs.

There has been in progress in this laboratory an investigation (8–10) of the metal complexes of the cycloheptatrienones. For the simple substitution products of tropolone, it was found that the stabilities of the complexes of a given metal (log K_{av}) are proportional to the pK_A values of the tropolones acting as weak acids. This relationship is interpreted as indicating that, in at least some respects, the nature of the chelate ring is independent of the ion through which the ring is closed. For a given pK_A value, the stabilities of the metal derivatives of the benzotropolones are less than those of the simple substituted tropolones. This fact is consistent with the hypothesis of Calvin and Wilson (11) concerning the resonance interference of aromatic rings fused to a chelate ring. It was thought advisable to investigate hydrogen bonding in the hope of shedding some light on the whole phenomenon of chelation.

For the cycloheptatrienones, it appeared that at least four factors might influence the stability of the chelate ring:



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1. The nature of atom Y.
2. The nature of atom X.
3. The nature and position of ring substituent Z.
4. The size of the chelate ring. (to be discussed in a subsequent publication.)

The discussions of the infrared spectra of tropolone and related compounds include little on carbonyl frequencies. For discussion of various features of the spectra of some tropolones, the work of Aulin-Erdtman and Theorell (12), Scott and Tarbell (13), and Kuratani, *et al.* (14) is outstanding.

EXPERIMENTAL

The organic compounds were prepared by methods described in other publications as indicated in Tables III–V. The authors wish to acknowledge the gifts of the α- and β-isopropyltropolones, 3,4-benzotropolone, and a hydroxytropolone by Professor T. Nozoe of the Tohoku University, Sendai, Japan; the γ-isopropyltropolone by Dr. W. M. Hearon of the Crown-Zellerbach Co., and the nootkatin (β-isopropyl-γ-(3-methylbut-2-enyl)tropolone) by Professor H. Erdtman of the Kungl. Tekniska Högskalan, Stockholm, Sweden.

Zinc tropolonate. A solution of 1 g. of tropolone in *ca.* 75 ml. of 95% ethanol was refluxed for 48 hr. with 1 g. of zinc oxide. The solid was filtered and extracted with dimethylformamide. Addition of water to the extract caused precipitation of a yellow solid. This material, when recrystallized from aqueous dimethylformamide, formed hexagonal plates, m.p. 280°.

Anal. Calc'd for $Zn(C_7H_5O_2)_2$: C, 54.65; H, 3.25.
Found: C, 54.51; H, 3.31.

Lead tropolonate. A solution of 1 g. of tropolone in 50 ml. of benzene was refluxed overnight with 3 g. of $PbCO_3$. The solution was filtered and evaporated and the residue was recrystallized twice from benzene-acetone to yield yellow needles, m.p. 228°.

Anal. Calc'd for $Pb(C_7H_5O_2)_2$: C, 37.42; H, 2.23.
Found: C, 37.48; H, 2.08.

Beryllium tropolonate. A solution of 1 g. of tropolone in 50 ml. of benzene was refluxed for 7 hr. with 0.1 g. of BeO. The filtered solution was evaporated and the residue was crystallized from aqueous acetone to yield sand-colored plates, m.p. 214°.

Anal. Calc'd for $Be(C_7H_5O_2)_2$: C, 66.93; H, 3.98.
Found: C, 66.83; H, 4.02.

Cadmium tropolonate. Addition of a methanolic solution of tropolone to a methanolic solution of $Cd(C_2H_3O_2)_2$ resulted in immediate precipitation of a cream-colored powder, m.p. > 275°, insoluble in the usual solvents. This material was ground under H_2O and then under acetone in an attempt to remove impurities.

Anal. Calc'd for $Cd(C_7H_5O_2)_2$: C, 47.40; H, 2.82.
Found: C, 46.68; H, 3.15.

TABLE I

METAL DERIVATIVES OF γ-ISOPROPYLTROPOLONE

Formula	Color	m.p., °C.	Analysis			
			C		H	
			Calc'd	Found	Calc'd	Found
$Co(C_{10}H_{11}O_2)_2$	Dark red	>275	62.34	61.49	5.76	5.26
$Cu(C_{10}H_{11}O_2)_2$	Green	267	61.60	62.52	5.69	6.07
$Zn(C_{10}H_{11}O_2)_2$	Sand	>280	61.31	60.62	5.62	5.97
$Cd(C_{10}H_{11}O_2)_2$	Yellow	>280	55.74	54.39	5.01	5.06

TABLE II

METAL DERIVATIVES OF BROMOTROPOLONE

Formula	Color	m.p., °C.	Analysis			
			C		H	
			Calc'd	Found	Calc'd	Found
$Be(C_7H_4BrO_2)_2$	Yellow	>250	41.08	40.66	1.97	2.24
$Zn(C_7H_4BrO_2)_2$	Yellow	>250	36.12	36.40	1.73	1.65
$Cd(C_7H_4BrO_2)_2$	Yellow	>250	32.81	32.63	1.57	1.62
$Pb(C_7H_4BrO_2)_2$	Yellow	232–235 (d)	27.69	24.60	1.31	1.71

TABLE III

THE EFFECT OF ATOM Y ON THE POSITION OF THE CARBONYL PEAK

Compound	Preparation (Reference No.)	Phase	C=O (μ)	Other prominent peaks in the range 6.0–7.0 μ	
Tropolone methyl ether	19	Dioxane soln.	6.14	6.28	6.67
2-Chlorotropone	20	Dioxane soln.	6.13	6.25	6.65
		CCl_4 soln.	6.11	6.23	6.65
Tropolone	18	Dioxane soln.	6.20	6.40	6.80
		CCl_4 soln.	6.19	6.40–6.45	6.70 and 6.80
Beryllium tropolonate		Dioxane soln.	6.25	6.51	7.02
Zinc tropolonate		Dioxane soln. (sat'd)	6.28		6.63
		Nujol mull	6.27	6.36	6.62
Lead tropolonate		Dioxane soln.	6.28		6.66
		Nujol mull	6.30		6.67
Palladium tropolonate	9	Nujol mull	6.30		6.62
Copper tropolonate	17	Nujol mull	6.28		6.60
Iron(III) tropolonate	17	Nujol mull	6.28		6.59
Manganese(II) tropolonate		Nujol mull	6.28	6.37	6.61
Cadmium tropolonate		Nujol mull	6.26	6.37	6.63

TABLE IV

THE EFFECT OF ATOM X ON THE POSITION OF THE CARBONYL PEAK

Compound	Preparation (Reference No.)	Phase	C=O (μ)	Other Prominent Peaks	
2-Aminotropone	19	Dioxane soln.	6.26	6.52	7.00
2-Hydrazinotropone	20	Dioxane soln.	6.23 and 6.28	6.43	6.66
2-Mercaptotropone		Dioxane soln.	6.36		6.82
		Cyclohexane soln.	6.35	6.62	6.83
		CCl_4 soln.	6.36	6.62	6.83
Lead 2-mercaptotroponate		Nujol mull	6.25	6.45	
Nickel 2-mercaptotroponate		Nujol mull	6.29	6.41–6.49	

TABLE V

THE EFFECT OF RING SUBSTITUENTS ON THE POSITION OF THE CARBONYL PEAK

Compound	Preparation (Reference No.)	Phase	$C{=}O$ (μ)	Other Prominent Peaks	
α-Methyltropolone	10	Dioxane soln.	6.21	6.43	6.75
	—	CCl_4 soln.k	6.19	6.45	6.70 and 6.76
β-Methyltropolone	10	Dioxane soln.	6.21	6.45	6.8 (broad)
		CCl_4 soln.	6.19	6.47	6.80
α-Isopropyltropolone		Dioxane soln.	6.19 and 6.25	6.45	6.75
		CCl_4 soln.	6.18	6.45	6.82
Lead α-isopropyltropolonate	10	Nujol mull	6.27		6.68
β-Isopropyltropolone		Dioxane soln.	6.21	6.45	6.80
		CCl_4 soln.	6.19	6.45	6.82
γ-Isopropyltropolone		Dioxane soln.	6.17	6.35	6.81
		CCl_4 soln.	6.15	6.40	6.80
Copper γ-isopropyltropolonate		Nujol mull	6.24	6.56	
Cobalt γ-isopropyltropolonate		Nujol mull	6.23	6.58	
Zinc γ-isopropyltropolonate		Nujol mull	6.24	6.60	
Cadmium γ-isopropyltropolonate		Nujol mull	6.22	6.56	6.81
β - Isopropyl - γ - (3 - methylbut - 2 - enyl)tropolone		Dioxane soln.	6.18	6.41	6.76
		CCl_4 soln.	6.16	6.40	6.73
α-Bromotropolone	18	Dioxane soln.	6.23–6.25	6.40	6.79
Lead α-bromotropolonate		Nujol mull	6.33		6.68
Cadmium α-bromotropolonate		Nujol mull	6.31		
Zinc α-bromotropolonate		Nujol mull	6.26		6.62
Beryllium α-bromotropolonate		Nujol mull	6.27		6.55
?-Hydroxytropolone[a]		Dioxane soln.	6.23	6.48	6.61
		CCl_4 soln.	6.26	6.50 + 6.56	6.98
3,4-Benzotropolone	20	CCl_4 soln.	6.25	6.43	
4,5-Benzotropolone	21	CCl_4 soln.	6.23	6.32	
Trimethylpurpurogallin	23	Dioxane soln.	6.29	6.47	6.61
Dimethylpurpurogallin	23	Dioxane soln.	6.25 and 6.31	6.44	7.10
Purpurogallin	22	Dioxane soln.	6.28 and 6.38	6.75	7.02

[a] This compound, m.p. 136–137°, is reported by Nozoe, Seto, Ito, Soto, and Katono, *Proc. Japan Acad.*, **28**, 488 (1952).

Manganese tropolonate was prepared in the same manner as the cadmium compound with the exception that one drop of ammonia was added to the solution. The resulting precipitate was an orange powder, m.p. > 280°, insoluble in the usual solvents.

Anal. Calc'd for $Mn(C_7H_5O_2)_2$: C, 56.57; H, 3.39.

Found: C, 55.72; H, 3.39.

Preparations and properties of the *iron* (18), *copper* (18), and *palladium* (9) tropolonates have already been described.

The *metal derivatives* of γ-isopropyltropolone were prepared in the same manner as the corresponding tropolone derivatives. Physical properties and analyses are given in Table I.

The *bromotropolonates* were prepared by the addition of an alcoholic solution of sodium bromotropolonate to an aqueous solution of the metal acetates. Because of the limited solubilities of these materials, they were purified by grinding under acetone and water. Physical properties and analyses are shown in Table II.

The *lead* derivative of 2-mercaptotropone was prepared by adding an aqueous solution of $Pb(NO_3)_2$ to a solution of 2-mercaptotropone in dioxane. The orange powder was found to decompose below 250°.

Anal. Calc'd for $Pb(C_7H_5OS)_2$: C, 34.91; H, 2.08.
Found: C, 35.14; H, 1.87.

The *nickel* derivative was prepared in a similar fashion. The reddish-purple plates melted at 273°.

Anal. Calc'd for $Ni(C_7H_5OS)_2$: C, 50.50; H, 3.01.
Found: C, 50.76; H, 3.07.

All spectra were taken on a Perkin-Elmer Model 21 recording infrared spectrophotometer. The dioxane used as solvent was purified by distillation from sodium and its spectrum was taken. It was found to be transparent in the region 5.9–6.5 μ. Other solvents used were Eastman Kodak Spectro-Grade materials.

The spectral data are presented in Tables III–V, arranged in the order of the three factors mentioned previously which would be expected to affect the nature of the chelate ring.

DISCUSSION

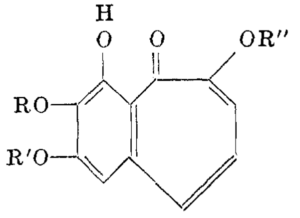
In order to evaluate the magnitude of the shifts caused by the various factors investigated, it was first necessary to determine the position of the carbonyl-group-absorption in compounds of cycloheptatrienone in which the chelate ring is absent. Doering and Detert report (15) that cycloheptatrienone itself absorbs at 1638 cm^{-1} (6.11μ). The 2-chlorotropone and tropolone methyl ether absorb in the region 6.11–6.14μ as shown in Table III. The shift toward longer wave lengths when compared with the C=O frequency of aliphatic ketones is adequately explained by the extended conjugation combined with the known highly ionic nature of the carbon-oxygen bond in tropone.

In compounds in which chelate ring formation is expected, a very noticable shift to longer wave-lengths is observed. From Tables III and IV, it is seen that wherever there is the possibility of the formation of a five-membered chelate ring closed through an hydroxyl hydrogen, the C=O absorption is shifted to about 6.20μ. Within the limits of the instrument as used (±0.015μ), this band is constant for tropolone and the alkyltropolones with the exception of those compounds having alkyl substituents in the γ-position. In these cases (γ-isopropyltropolone, nootkatin, and the metal derivatives of γ-isopropyltropolone) the carbonyl band appears at noticeably shorter wave lengths. Where the chelate ring is closed through some element other than hydrogen, however, the shift is markedly greater. Within the accuracy of the data, no correlation between the observed shifts and the values of the formation constants is possible. It should be noted that where the atom closing the ring is beryllium, the shift is the least, while for lead and palladium the shift is the greatest. Construction of Taylor-Fisher-Hershfelder models indicates that considerable strain will exist in the five-membered chelate ring of tropolone unless the "closing atom" is at least as large as the Co(III) ion. The beryllium and hydrogen ions have a further similarity in the great differences in subsequent electronic orbitals. It is apparent, however, that factors other than those mentioned affect the stability of the coordination compounds, since, for example, the formation constant of beryllium tropolonate is greater than that of the zinc or lead compound.

Table IV shows that the nature of atom X very definitely affects the C═O frequency. The shift of the carbonyl frequency in 2-mercaptotropone together with the absence of absorption in the region around 3.8–3.9μ due to SH indicates that the H of the SH may form a hydrogen bond with the O of the carbonyl group.[3] Molecular models indicate that the very large sulfur atom of 2-mercaptotropone permits formation of the five-membered ring closed through hydrogen with practically no strain. The appreciably lower negativity of the sulfur must affect the nature of the hydrogen-oxygen link also. The very pronounced shift of the carbonyl frequency in 2-mercaptotropone must be contrasted with the position of the carbonyl peak in the lead and nickel derivatives. These are the only cases noted in this study in which the carbonyl frequency of the hydrogen compound is found at a longer wave length than that for the metal derivatives. There are at least two apparent factors which might cause such an inversion: (a) both lead and nickel have a pronounced affinity for sulfur, which conceivably could affect the strength of the metal-oxygen bond, and (b) ring strain may be introduced when a large metal ion as well as the large sulfur are incorporated in a five-membered ring. An evaluation of the 2-aminotropone and 2-hydrazinotropone data is more difficult due to the multiplicity of hydrogens capable of bonding with the oxygen. In 2-hydrazinotropone, the possibilities of both five- and six-membered rings must be considered. This might explain the existence of two distinct peaks at 6.23μ and 6.28μ. Again, the electronegativity difference of oxygen and nitrogen must not be overlooked. In contrast to 2-aminotropone with peaks at 2.97 and 3.07μ, 2-hydrazinotropone has only one peak in the 3μ region at 3.13μ.

Table V shows that the effect of alkyl substitution on the tropolone nucleus is small. The electron-attracting Br and OH substituents have a small, but noticable, effect of increasing the frequency of absorption.

The purpurogallins are represented by the general structure:



Purpurogallin: $R = R' = R'' = H$

Dimethylpurpurogallin: $R = R' = CH_3, R'' = H$

Trimethylpurpurogallin: $R = R' = R'' = CH_3$

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[3] A general study of the ability of the SH group to form intramolecular hydrogen bonds (chelate rings) with C═O is in progress.

In the spectrum of trimethylpurpurgallin a single intense band at 6.29μ is observed. This compound is capable of forming only one chelate ring of six members and closed through a hydrogen atom. Purpurogallin and dimethylpurpurogallin show two peaks each, both at exceptionally long wave lengths. Thorn and Barclay (16) by a study of the ultraviolet spectra have concluded that the stronger hydrogen bond is that in the six-membered ring, although the possibility exists for the formation of a five-membered ring. Bryant and Fernelius (17) have suggested that in purpurogallin and dimethylpurpurogallin it is probable that the carbonyl oxygen is common to *two* chelate rings: one five-membered and one six-membered. The existence of two distinct peaks seems to lend support to this suggestion. The rather complex nature of these molecules makes any speculation concerning the extremely long wave lengths very uncertain. Other data (9) indicate that the large number of oxygen atoms in the methoxy and hydroxy groups should certainly tend to lengthen the wave-length of absorbed light.

The spectra of all the compounds reported here show gross differences only in the long (10–15μ) region. It can be seen from Tables III–V that in the region of interest, only slight differences are caused by using different solvents. For the metal complexes, Nujol mulls were found most satisfactory because of the very limited solubilities of these compounds.

We are indebted to Nils C. Fernelius for making a number of the infrared spectrograms.

SUMMARY

The infrared spectra of 38 compounds containing the cycloheptatrienone nucleus have been examined with particular attention to the absorption by the carbonyl group. These include tropolone and its metal salts; compounds in which the OH of tropolone is replaced by Cl, OCH_3, NH_2, $NHNH_2$, and SH; simple substitution products of tropolone; and the benzotropolones. Syntheses and properties of some of the metal complexes have been described.

Formation of a chelate ring invariably causes a shift of the carbonyl frequency to longer wave lengths. The magnitude of the shift is dependent on the nature of the atoms in the chelate ring and the substituents on the cycloheptatrienone nucleus. In cases where the formation of two chelate rings of different sizes is possible, two carbonyl frequencies are observed.

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